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Susumu KANZAKI, et al.

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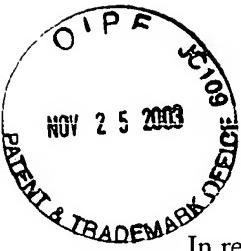
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Filed: March 05, 2002

For: POLYPROPYLENE-BASED RESIN COMPOSITION, PROCESS FOR PRODUCING  
THE SAME, AND INJECTION MOLDED ARTICLE

**SWORN ENGLISH TRANSLATION OF  
PRIORITY DOCUMENT**

**JAPANESE PATENT APPLICATION NO. 2001-063020**

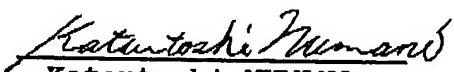


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### D E C L A R A T I O N

I, Katsutoshi NUMANO, a national of Japan, c/o Sumitomo Chemical Intellectual Property Service, Limited, 5-33, Kitahama 4-chome, Chuo-ku, Osaka-shi, Osaka 541-8550, Japan, declare that to the best of my knowledge and belief the attached is a full, true and faithful translation into English made by me of the certified copy of Japanese Patent Application No. 2001-063020 attached thereto.

Signed this 21st day of November, 2003

  
Katsutoshi NUMANO

PATENT OFFICE  
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy of the following application as filed with this Office.

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Applicant(s) : SUMITOMO CHEMICAL COMPANY, LIMITED

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[Title of the Invention] Polypropylene-based resin composition, method of producing the same and injection molded body made of the same

[Claims]

[Claim 1] A polypropylene-based resin composition comprising 0.5 to 10% by weight of a propylene-based polymer component (A1) obtained by polymerizing a monomer mainly composed of propylene having a limiting viscosity  $[\eta]^{A1}$  of 5 dl/g or more and a melting temperature peak  $T_m^{A1}$  in a temperature rising thermogram by a differential scanning calorimeter (DSC) of 130 to 160°C, and 90 to 99.5% by weight of a propylene-based polymer component (A2) obtained by polymerizing a monomer mainly composed of propylene having a limiting viscosity  $[\eta]^{A2}$  of less than 5 dl/g.

[Claim 2] The polypropylene-based resin composition according to Claim 1 wherein the propylene-based polymer component (A2) comprises 50 to 94.5% by weight of a propylene polymer component (B) having a limiting viscosity  $[\eta]^{B_p}$  of 1.5 dl/g or less and 5 to 40% by weight of a propylene-ethylene random copolymer component (C) having a limiting viscosity  $[\eta]_{EP}^{C_p}$  of 8 dl/g or less and an ethylene content of 20 to 70% by weight.

[Claim 3] The polypropylene-based resin composition according to Claim 1 wherein the propylene-based polymer component (A2) is a polypropylene-based resin (D) constituted of a propylene

polymer component (B) having a limiting viscosity  $[\eta]_{sp}^B$  of 1.5 dl/g or less, selected from propylene-ethylene block copolymers (i) and mixtures (iii) of said propylene-ethylene block copolymers (i) and propylene polymers (ii) and a propylene-ethylene random copolymer component (C) having a limiting viscosity  $[\eta]_{sp}^C$  of 8 dl/g or less and an ethylene content of 20 to 70% by weight.

[Claim 4] The polypropylene-based resin composition according to Claim 1 or 3 wherein the content of the propylene-based polymer component (A1) is from 0.52 to 9.8% by weight and the propylene-based polymer component (A2) comprises 0.78 to 4.2% by weight of the propylene polymer component (B) and 98.7 to 86% by weight of a polypropylene-based resin (D).

[Claim 5] The polypropylene-based resin composition according to Claim 1 wherein the propylene-based polymer component (A1) has a limiting viscosity  $[\eta]_{sp}^{A1}$  of 6 to 9 dl/g and a melting temperature peak  $T_m^{A1}$  in a temperature rising thermogram by a differential scanning calorimeter (DSC) of 135 to 155°C.

[Claim 6] The polypropylene-based resin composition according to Claim 1 wherein the propylene-based polymer component (A1) is a random copolymer of propylene and ethylene, having an ethylene content of 1 to 7% by weight.

[Claim 7] The polypropylene-based resin composition according to Claim 2 or 3 wherein the propylene polymer component (B) has a limiting viscosity  $[\eta]_{sp}^B$  of 0.7 to 1.5 dl/g and the

propylene-ethylene random copolymer component (C) has a limiting viscosity  $[\eta]_{\text{EP}}^{\text{C}}$  of 1.5 to 4 dl/g.

[Claim 8] The polypropylene-based resin composition according to any of Claims 1 to 7 wherein the polypropylene-based resin composition has a melt flow rate (MFR) of 5 to 150 g/10 minutes.

[Claim 9] The polypropylene-based resin composition according to any of Claims 1 to 7 wherein the polypropylene-based resin composition has a molecular weight distribution Q value (Mw/Mn) measured by GPC of less than 10.

[Claim 10] The polypropylene-based resin composition according to any of Claims 1 to 7 wherein the polypropylene-based resin composition has a die swell (D. S.) of 1.6 or more.

[Claim 11] A polypropylene-based resin composition comprising 35 to 88% by weight of the polypropylene-based resin composition according to any of Claims 1 to 10, 0 to 20% by weight of a propylene homopolymer (F), 10 to 35% by weight of an elastomer (G) and 2 to 30% by weight of an inorganic filler(H).

[Claim 12] An injection molded body made of the polypropylene-based resin composition according to any of Claims 1 to 11.

[Claim 13] A method of producing the polypropylene-based resin composition according to Claim 4, comprising mixing 98.7 to 86% by weight of the polypropylene-based resin (D) with 1.3 to 14% by weight of a propylene-based polymer composition (E) composed of 40 to 70% by weight of the propylene-based polymer

component (A1) and 60 to 30% by weight of the propylene polymer component (B).

[Detailed Description of the Invention]

(0001)

[Field of the Invention]

The present invention relates to a polypropylene-based resin composition, a method of producing the same and an injection molded body made of the same. More particularly, the present invention relates to a polypropylene-based resin composition which, when made into a molded body, has a low tendency of generation of flow marks, namely, has excellent appearance such as low die swell, little generation of granular structures and the like, and is excellent in balance of rigidity and toughness, a method of producing the same and an injection molded body made of the same.

(0002)

[Prior Art]

Polypropylene-based resin compositions are materials excellent in rigidity, impact resistance and the like, and utilized in wide applications as molded bodies such as automobile interior and exterior materials, electric parts housings and the like. It is conventionally well known that, of these polypropylene-based resin compositions, polypropylene-based resin compositions comprising a propylene-ethylene block

copolymer, for example, polypropylene-based resin compositions composed of a propylene-ethylene block copolymer and a propylene homopolymer, or of different two or more propylene-ethylene block copolymers, are excellent in rigidity, impact resistance and the like and suitably used.

(0003)

For example, JP-A-7-157626 describes a thermoplastic resin composition containing a propylene-ethylene block copolymer obtained by multi-stage polymerization and polyolefin-based rubber. As the propylene-ethylene block copolymer, those composed of a propylene-ethylene block copolymer having a propylene-ethylene random copolymerization phase having an ethylene content of from 5 to 50% by weight and a limiting viscosity of from 4.0 to 8.0 dl/g and a propylene-ethylene block copolymer having an ethylene content of over 50% by weight and 98% by weight or less and a limiting viscosity of 2.0 dl/g or more and less than 4.0 dl/g are used, and it is described that a thermoplastic resin composition having extremely high ductility is obtained.

(0004)

JP-A-7-157627 describes a thermoplastic resin composition containing a propylene-ethylene block copolymer obtained by multi-stage polymerization and polyolefin-based rubber. As the propylene-ethylene block copolymer, those composed of a block copolymer having a propylene-ethylene random

copolymerization phase having a limiting viscosity of from 4.0 to 8.0 dl/g and a block copolymer having a limiting viscosity of 2.0 dl/g or more and less than 4.0 dl/g are used (excluding a propylene-ethylene block copolymer having a propylene-ethylene random copolymerization phase having a limiting viscosity of from 4.0 to 8.0 dl/g and an ethylene content of from 5 to 50% by weight and a propylene-ethylene block copolymer having a limiting viscosity of 2.0 dl/g or more and less than 4.0 dl/g and an ethylene content of over 50% by weight and 98% by weight or less), and it is described that a thermoplastic resin composition having extremely high ductility is obtained.

(0005)

JP-A-7-233305 describes a polypropylene resin composition having improved melt index, composed of a polypropylene, inorganic fillers and a metal soap of a fatty acid constituted of 15 to 20 carbon atoms and zinc. As the polypropylene, block copolymers containing a propylene-ethylene copolymerization part having a  $[\eta]$  of 2 to 6 dl/g and a propylene-ethylene copolymerization part having a  $[\eta]$  of 7 to 15 dl/g are described, and as a preferable embodiment, those composed of at least two kinds of block copolymers are described. Further, it is described that a polypropylene resin composition is obtained, manifesting no practically problematical lowering in impact strength, rigidity, heat

resistance and the like, having improved flowability and suitable for producing a thickness-reduced molded article, and showing little discoloration to yellow and pink and little embossment on the surface of a mold and the surface of an injection molded article caused by pelletizing.

(0006)

A propylene-ethylene block copolymer suitably used due to excellent rigidity, impact resistance and the like is produced, recently, by a continuous gas phase method using a simple production process and realizing production at low cost. However, a propylene-ethylene block copolymer produced by a gas phase method generally has problems of occurrence of granular structure and poor appearance of a molded body when the limiting viscosity of a propylene-ethylene random copolymer portion is set at high level.

(0007)

For solving such problems on appearance, for example, JP-A-7-286075 describes a propylene polymer composition composed of a propylene polymer produced by a continuous polymerization method in which the 23°C n-decane-soluble component content is 0% by weight or more and less than 15% by weight and this 23°C n-decane-soluble component contains a structural unit derived from ethylene in an amount of 30 to 60 mol% and has a limiting viscosity [ $\eta$ ] of 3 to 7 dl/g, and a propylene block copolymer produced by a batch-wise solvent

polymerization method or continuous solvent polymerization method in which the 23°C n-decane-soluble component content is 15 to 40% by weight and this 23°C n-decane-soluble component contains a structural unit derived from ethylene in an amount of 30 to 60 mol% and has a limiting viscosity [ $\eta$ ] of 5 to 12 dl/g, and it is described that a propylene polymer composition having excellent rigidity and impact resistance and capable of forming a molded article without generating granular structure on appearance is obtained, however, there is desired a further improvement regarding generation of granular structures.

(0008)

On the other hand, WO98/54233 describes a polypropylene resin composition in which the content of a high molecular weight polypropylene having a limiting viscosity [ $\eta$ ] of 9 to 13 dl/g is from 15 to 30% by weight, the molecular weight distribution represented by  $M_w/M_n$  is 20 or more, the molecular weight distribution represented by  $M_z/M_w$  is 7 or more, and when molded into an injection molded article, the thickness of a skin layer formed on the surface of this injection molded article is 300  $\mu m$  or more, and it is described that a polypropylene resin composition which has light weight, has extremely high rigidity and heat resistance and manifests excellent flowability in molding and excellent in processability can be produced.

(0009)

However, it is described in, for example, Plastics Age, May, 1980, p. 93, Fig. 2. 27 that when the thickness of a skin layer formed on the surface of an injection molded article increases, ultimate elongation (tensile elongation), namely, toughness lowers, and there is a desire for an improvement of balance between rigidity and toughness regarding the above-mentioned polypropylene resin composition described in WO98/54233.

(0010)

JP-A-2000-226478 describes a polypropylene resin composition having a molecular weight distribution represented by  $M_w/M_n$  of 8 or more, comprising a high molecular weight polypropylene having a limiting viscosity [ $\eta$ ] of 6 to 11 dl/g and a low molecular weight polypropylene having a limiting viscosity [ $\eta$ ] of 0.6 to 1.6 dl/g, and it is described that a polypropylene resin composition which has light weight, has extremely high rigidity and heat resistance and, shows excellent flowability in molding, generates no cracking in molding and excellent in molding property can be provided. However, since the ultimate elongation of the above-mentioned polypropylene resin composition described in an example of JP-A-2000-226478 is from 8 to 16%, there is desired an improvement in balance between rigidity and toughness.

(0011)

As described above, there is a desire for the development

of a polypropylene-based resin composition which, when molded into a molded body, manifests a low tendency of generation of flowmark on the surface of the molded body, namely, has excellent appearance properties such as high die swell and practically no-problematical generation of granular structures, and excellent in balance between rigidity and toughness.

(0012)

[Problems to be solved by the Invention]

An object of the present invention is to provide a polypropylene-based resin composition which, when molded into a molded body, manifests a low tendency of generation of flow mark, namely, has excellent appearance properties such as high die swell, generation of little granular structure, and the like, and excellent in balance between rigidity and toughness, a method of producing the same, and an injection molded body made of the same.

(0013)

[Means for solving the Problems]

The present inventors have intensively studies in view of such practical conditions, and resultantly found that the above-mentioned problems can be solved by a polypropylene-based resin composition comprising a propylene-based polymer component obtained by polymerizing a monomer mainly composed of propylene, having limiting viscosity in a specific range and a melting temperature peak in a temperature rising thermogram

by a differential scanning calorimeter (DSC) in a specific range and of which content is in a certain range and a propylene-based polymer component obtained by polymerizing a monomer mainly composed of propylene, having limiting viscosity in a specific range and of which content is in a certain range, a method of producing the same, and an injection molded body made of the same, leading to completion of the present invention.

(0014)

Namely, the present invention relates to a polypropylene-based resin composition comprising 0.5 to 10% by weight of a propylene-based polymer component (A1) obtained by polymerizing a monomer mainly composed of propylene having a limiting viscosity [ $\eta$ ]<sup>A1</sup> of 5 dl/g or more and a melting temperature peak  $T_m^{A1}$  in a temperature rising thermogram by a differential scanning calorimeter (DSC) of 130 to 160°C, and 90 to 99.5% by weight of a propylene-based polymer component (A2) obtained by polymerizing a monomer mainly composed of propylene having a limiting viscosity [ $\eta$ ]<sup>A2</sup> of less than 5 dl/g, a method of producing the same, and an injection molded body made of the same.

The present invention will be described in detail below.

(0015)

#### [Mode for Carrying out the Invention]

The propylene-based polymer component (A1) used in the present invention is a propylene-based polymer obtained by

polymerizing a monomer mainly composed of propylene, and examples thereof include a propylene homopolymer obtained by homopolymerization of propylene, a propylene-ethylene random copolymer obtained by copolymerization of propylene and ethylene, a propylene- $\alpha$ -olefin random copolymer obtained by copolymerization of propylene and an  $\alpha$ -olefin having 4 to 12 carbon atoms, and the like, and preferable is a propylene-ethylene random copolymer.

(0016)

The content of a propylene-ethylene random copolymer is usually from 0.5 to 8% by weight, preferably from 1 to 7% by weight.

(0017)

As the  $\alpha$ -olefin having 4 to 12 carbon atoms used in a propylene-ethylene random copolymer, butene-1, pentene-1, hexene-1, 4-methylpentene-1, octane-1, decene-1 and the like are listed, and preferable is butene-1.

The content of the  $\alpha$ -olefin is usually from 1 to 20% by weight, preferably from 2 to 15% by weight.

(0018)

As the propylene- $\alpha$ -olefin random copolymer, for example, a propylene-butene-1 random copolymer, propylene-hexene-1 random copolymer and the like are listed, and preferable is a propylene-butene-1 random copolymer.

(0019)

The limiting viscosity  $[\eta]^{A1}$  of the propylene-based polymer component (A1) used in the present invention is 5 dl/g or more, preferably 6 dl/g or more, and from the standpoint of dispersibility of the component (A1), further preferably 6 to 9 dl/g. When the limiting viscosity  $[\eta]^{A1}$  is less than 5 dl/g, high die swell is not obtained, and flow mark may be insufficient in some cases.

(0020)

The melting temperature peak  $Tm^{A1}$  in a temperature rising thermogram by a differential scanning calorimeter (DSC) of the propylene-based polymer component (A1) used in the present invention is from 130 to 160°C, preferably from 135 to 155°C. When  $Tm^{A1}$  is less than 130°C, high rigidity may not be obtained, and when over 160°C, sufficient tensile elongation may not be obtained, and due to insufficient dispersion of the component (A1), a lot of granular structure may be formed.

(0021)

The propylene-based polymer component (A2) used in the present invention is a propylene-based polymer component obtained by polymerizing a monomer mainly composed of propylene, and specific examples thereof include a propylene homopolymer obtained by homopolymerization of propylene, a propylene-ethylene random copolymer obtained by copolymerization of propylene and ethylene, a propylene- $\alpha$ -olefin random copolymer obtained by copolymerization of

propylene and an  $\alpha$ -olefin having 4 to 12 carbon atoms, and the like, as in the case of the above-mentioned propylene-based polymer component (A1), and also as the  $\alpha$ -olefin having 4 to 12 carbon atoms, the same compounds as listed above are mentioned.

The limiting viscosity  $[\eta]^{A2}$  of the propylene-based polymer component (A2) used in the present invention is less than 5 dl/g.

(0023)

When the content of the propylene-based polymer component (A1) is less than 0.5% by weight (namely, when the content of the propylene-based polymer component (A2) is over 99.5% by weight), high die swell is not obtained, and flow mark may be insufficient, and when the content of the propylene-based polymer component (A1) is over 10% by weight (namely, when the content of the propylene-based polymer component (A2) is less than 90% by weight), the melt flowrate (MFR) of the polypropylene resin composition lowers and flowability thereof may decrease.

(0024)

As the propylene-based polymer component (A2) used in the present invention, there are preferably listed from the standpoint of balance between rigidity and toughness of the polypropylene-based resin composition of the present invention, (A2-1) those comprising a propylene polymer component (B) having a limiting viscosity  $[\eta]^{B_p}$  of 1.5 dl/g or less and a

propylene-ethylene random copolymer component (C) having a limiting viscosity  $[\eta]_{EP}^C$  of 8 dl/g or less and an ethylene content of 20 to 70% by weight. (A2-2) polypropylene-based resins constituted of a propylene polymer component (B) having a limiting viscosity  $[\eta]_{EP}^B$  of 1.5 dl/g or less and a propylene-ethylene random copolymer component (C) having a limiting viscosity  $[\eta]_{EP}^C$  of 8 dl/g or less and an ethylene content of 20 to 70% by weight, selected from propylene-ethylene block copolymers (i) and mixtures (iii) of the propylene-ethylene block copolymers (i) and propylene polymers (ii), and (A2-3) those comprising the propylene polymer component (B) and the polypropylene-based resin (D) (0025)

Explanation of (A2-1) those comprising a propylene polymer component (B) and a propylene-ethylene random copolymer component (C):

The propylene polymer component (B) used in (A2-1) those comprising a propylene polymer component (B) and a propylene-ethylene random copolymer component (C) is a propylene homopolymer obtained by homopolymerization of propylene or a propylene- $\alpha$ -olefin random copolymer obtained by copolymerization of propylene and an  $\alpha$ -olefin having 4 to 12 carbon atoms. As the  $\alpha$ -olefin having 4 to 12 carbon atoms and propylene- $\alpha$ -olefin random copolymer, those listed above are specifically mentioned.

(0026)

The limiting viscosity  $[\eta]^B$ , of the propylene polymer component (B) used in (A2-1) is preferably 1.5 dl/g or less, further preferably from 0.7 to 1.5 dl/g from the standpoints of the melt flow rate (MFR) and flowability of a polypropylene-based resin composition.

(0027)

The isotactic pentad fraction calculated and measured using  $^{13}\text{C-NMR}$  of the propylene polymer component (B) used in (A2-1) is preferably 0.95 or more, further preferably 0.97 or more from the standpoints of rigidity, heat resistance and the like.

(0028)

The propylene-ethylene random copolymer component (C) used in (A2-1) those comprising a propylene polymer component (B) and a propylene-ethylene random copolymer component (C) is a propylene-ethylene random copolymer obtained by copolymerization of propylene and ethylene.

(0029)

The ethylene content  $[(\text{C}_2')_{EP}]$  in the propylene-ethylene random copolymer component (C) used in (A2-1) is preferably from 20 to 70% by weight, more preferably from 25 to 65% by weight, from the standpoint of impact resistance.

(0030)

The limiting viscosity  $[\eta]_{EP}^C$  of the propylene-ethylene

random copolymer component (C) used in (A2-1) is preferably 8 dl/g or less, more preferably 6 dl/g or less, further preferably 1.5 to 4 dl/g, from the standpoints of prevention of significant generation of granular structures on a molded article.

(0031)

The above-mentioned granular structure is a block mainly composed of a propylene-ethylene random copolymer component (C), generating due to poor dispersibility of the propylene-ethylene random copolymer component (C) in a polypropylene-based resin composition, and the size thereof is about 100 to several hundreds  $\mu\text{m}$ . In the case of formation of a molded article by injection molding and the like using a material containing a lot of granular structures, not only the appearance of the surface of the molded article is deteriorated but also reverse influences are exerted on mechanical properties such as impact resistance and the like.

(0032)

The compounding ratio of (A2-1) those comprising a propylene polymer component (B) and a propylene-ethylene random copolymer component (C) in the polypropylene-based resin composition of the present invention is from 90 to 99.5% by weight (namely, the compounding ratio of a propylene-based polymer component (A1) is from 0.5 to 10% by weight), and the compounding ratio of a propylene polymer component (B) used in (A2-1) is preferably from 50 to 94.5% by weight (namely,

the compounding ratio of a propylene-ethylene random copolymer component (C) is from 5 to 40% by weight), further preferably, the compounding ratio of a propylene polymer component (B) is from 60 to 94.5% by weight (namely, the compounding ratio of a propylene-ethylene random copolymer component (C) is from 5 to 30% by weight).

(0033)

Explanation of (A2-2) polypropylene-based resin (D), selected from propylene-ethylene block copolymers (i) and mixtures (iii) of the propylene-ethylene block copolymers (i) and propylene polymers (ii)

(0034)

The propylene-ethylene block copolymer (i) used in the polypropylene-based resin (D)(A2-2) is a propylene-ethylene block copolymer composed of a propylene polymer portion (referred to as first segment of copolymer (i)) and a propylene-ethylene random copolymer (referred to as second segment of copolymer (i)).

(0035)

The propylene polymer (ii) used in the polypropylene-based resin (D)(A2-2) is a propylene homopolymer obtained by homopolymerization of propylene or a propylene- $\alpha$ -olefin random copolymer obtained by copolymerization of an  $\alpha$ -olefin having 4 to 12 carbon atoms. As the  $\alpha$ -olefin having 4 to 12 carbon atoms and propylene- $\alpha$ -olefin random copolymer,

those listed above are specifically mentioned.

(0036)

When the polypropylene-based resin (D)(A2-2) is a mixture (iii) of the propylene-ethylene block copolymer (i) and propylene polymer (ii), the propylene polymer component (B) of the polypropylene-based resin (D) means both of a propylene polymer portion, the first segment of the propylene-ethylene block copolymer (i), and a propylene polymer (ii), and the propylene-ethylene random copolymer component (C) of the polypropylene-based resin (D) means a propylene-ethylene random copolymer portion, the second segment of the propylene-ethylene block copolymer (i).

(0037)

As the propylene-ethylene block copolymer (i) and propylene polymer (ii) used in the polypropylene-based resin (D)(A2-2), two or more propylene-ethylene block copolymers, two or more propylene polymers or mixtures thereof may be used, if necessary.

(0038)

The limiting viscosity  $[\eta]^B$ , of the propylene polymer component (B) constituting the polypropylene-based resin (D)(A2-2) is preferably 1.5 dl/g or less, further preferably from 0.7 to 1.5 dl/g from the standpoints of the melt flow rate (MFR) and flowability of a polypropylene-based resin composition.

(0039)

The isotactic pentad fraction calculated and measured using  $^{13}\text{C-NMR}$  of the propylene polymer component (B) constituting the polypropylene-based resin (D)(A2-2) is preferably 0.95 or more, further preferably 0.97 or more from the standpoints of rigidity, heat resistance and the like.

(0040)

The limiting viscosity  $[\eta]_{\text{sp}}^{\text{C}}$  of the propylene-ethylene random copolymer component (C) used in (A2-2) constituting the polypropylene-based resin (D)(A2-2) is preferably 8 dl/g or less, more preferably 6 dl/g or less, further preferably 1.5 to 4 dl/g, from the standpoints of prevention of significant generation of granular structures on a molded article.

(0041)

The above-mentioned granular structure is a block mainly composed of a propylene-ethylene random copolymer component (C), generating due to poor dispersibility of the propylene-ethylene random copolymer component (C) constituting the polypropylene-based resin (D)(A2-2), and the size thereof is about 100 to several hundreds  $\mu\text{m}$ . In the case of formation of a molded article by injection molding and the like using a material containing a lot of granular structures, not only the appearance of the surface of the molded article is deteriorated but also reverse influences are exerted on mechanical properties such as impact resistance and the like.

(0042)

The ethylene content [ $(C2')_{sp}$ ] in the propylene-ethylene random copolymer component (C) constituting the polypropylene-based resin (D)(A2-2) is preferably from 20 to 70% by weight, more preferably from 25 to 65% by weight, from the standpoint of impact resistance.

(0043)

Regarding the ratio of a propylene polymer component (B) to a propylene-ethylene random copolymer component (C), constituting the polypropylene-based resin (D)(A2-2), the ratio of a propylene-ethylene random copolymer component (C) is preferably from 5 to 40% by weight (namely, the ratio of a propylene polymer component (B) is from 95 to 60% by weight), further preferably, the ratio of a propylene-ethylene random copolymer component (C) is from 5 to 30% by weight (namely, the ratio of a propylene polymer component (B) is from 95 to 70% by weight) (wherein, the total amount of a propylene polymer component (B) and a propylene-ethylene random copolymer component (C) is 100% by weight).

(0044)

Explanation of (A2-3) those comprising a propylene polymer component (B) and a polypropylene-based resin (D)

As the propylene polymer component (B) and polypropylene-based resin (D) used in (A2-3) those comprising a propylene polymer component (B) and a polypropylene-based

resin (D), those used in the above-mentioned (A2-1) or (A2-2) are mentioned.

(0045)

Regarding the compounding ratio when (A2-3) those comprising a propylene polymer component (B) and a polypropylene-based resin (D) are used in the polypropylene-based resin composition of the present invention, preferably, the amount of the propylene-based polymer component (A1) is from 0.52 to 9.8% by weight, the amount of the propylene polymer component (B) is from 0.78 to 4.2% by weight, and the amount of the polypropylene-based resin (C) is from 98.7 to 86% by weight.

(0046)

The melt flow rate (MFR) of the polypropylene-based resin composition of the present invention is preferably from 5 to 150 g/10 minutes, more preferably from 10 to 120 g/10 minutes, from the standpoints of easiness in large scale molding, molding property, flow mark, or impact resistance.

(0047)

The molecular weight distribution Q value measured by GPC of the polypropylene-based resin composition of the present invention is preferably less than 10, more preferably from 3 to 8, further preferably from 3 to 7, from the standpoint of tensile elongation.

(0048)

The die swell (D. S.) of the polypropylene-based resin composition of the present invention is preferably 1.6 or more from the standpoint of flow mark generated on the surface of a molded article.

(0049)

The method of producing the polypropylene-based resin composition of the present invention is not particularly restricted, and exemplified are methods of obtaining a propylene-based polymer having a propylene-based polymer component (A1), preferably, a method (I) of obtaining a polypropylene-based resin composition as a propylene-based polymer having the above-mentioned propylene-based polymer component (A1), propylene polymer component (B) and propylene-ethylene random copolymer component (C), a method (II) of obtaining a polypropylene-based resin composition by melt-blending a propylene-based polymer partially having the propylene-based polymer component (A1), propylene polymer component (B) and propylene-ethylene random copolymer component (C), and other methods. Further, also the method of producing a propylene-ethylene block copolymer (i) and a propylene polymer (ii) used in a mixture (iii) is not particularly restricted, and the above-mentioned method (I) is preferably mentioned. Typical examples thereof are shown below.

(0050)

Explanation of a method (I) of obtaining a polypropylene-based resin composition as a propylene-based polymer having a propylene-based polymer component (A1), propylene polymer component (B) and propylene-ethylene random copolymer component (C)

The above-mentioned method (I) is not particularly restricted, and methods of obtaining a propylene-based polymer according to a known polymerization method using a known polymerization catalyst are listed.

As the known polymerization catalyst, for example, (a) solid catalyst components containing as an essential component, magnesium, titanium, halogen and electron donor, (b) organoaluminum compounds, and (c) catalyst systems formed of an electron donor component.

(0051)

(1) Catalyst system

(a) Solid catalyst component

(a-1) Titanium compound

As the titanium compound used for synthesis of a solid catalyst component (a), for example, titanium compounds of the general formula  $Ti(OR^1)_aX_{4-a}$  ( $R^1$  represents a hydrocarbon group having 1 to 20 carbon atoms, X represents a halogen atom, and a represents a number satisfying  $0 \leq a \leq 4$ .) are listed. Specific examples thereof include titanium tetrahalide compounds such as titanium tetrachloride and the like, alkoxytitanium

trihalide compounds such as ethoxytitanium trichloride, butoxytitanium trichloride and the like, dialkoxytitanium dihalide compounds such as diethoxytitanium dichloride, dibutoxytitanium dichloride and the like, trialkoxytitanium monohalide compounds such as triethoxytitanium chloride, tributoxytitanium chloride and the like, and tetraalkoxytitanium compounds such as tetraethoxytitanium, tetrabutoxytitanium and the like. These titanium compounds may be used alone or in combination of two or more.

(0052)

(a-2) Organosilicon compound having Si-O bond

As the organosilicon compound used for synthesis of a solid catalyst component (a), for example, silicon compounds of the general formula  $R^2_nSi(OR^3)_{4-n}$  ( $R^2$  represents a hydrocarbon group having 1 to 20 carbon atoms or a hydrogen atom, and  $R^3$  represents a hydrocarbon group having 1 to 20 carbon atoms.  $n$  represents a number satisfying  $0 \leq n < 4$ .) are listed. Specific examples thereof include tetraalkoxysilanes such as tetramethoxysilane, tetraethoxysilane, tetrabutoxysilane and the like, alkyltrialkoxysilanes such as methyltrimethoxysilane, ethyltrimethoxysilane, butyltrimethoxysilane, isobutyltrimethoxysilane, t-butyltrimethoxysilane, methyltriethoxysilane, ethyltriethoxysilane, butyltriethoxysilane, isobutyltriethoxysilane, t-butyltriethoxysilane and the like, dialkyldialkoxysilanes

such as dimethyldimethoxysilane, diethyldimethoxysilane, dibutyldimethoxysilane, diisobutyldimethoxysilane, di-t-butyldimethoxysilane, butylmethyldimethoxysilane, butylethyldimethoxysilane, t-butylmethyldimethoxysilane, dimethyldiethoxysilane, diethyldiethoxysilane, dibutyldiethoxysilane, diisobutyldiethoxysilane, di-t-butyldiethoxysilane, butylmethyldiethoxysilane, butylethyldiethoxysilane, t-butylmethyldiethoxysilane and the like, and other silicon compounds.

(0053)

#### (a-4) Ester compounds

As the ester compound used for synthesis of a solid catalyst component (a), for example, mono and polyvalent carboxylates are used, and aliphatic carboxylates, alicyclic carboxylates and aromatic carboxylates are exemplified. Specific examples thereof include methyl acetate, ethyl acetate, methyl propionate, ethyl propionate, ethyl butyrate, ethyl valerate, methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl benzoate, butyl benzoate, methyl toluate, ethyl toluate, ethyl anisate, diethyl succinate, dibutyl succinate, diethyl malonate, dibutyl malonate, dimethyl maleate, dibutyl maleate, diethyl itacoante, dibutyl itaconate, diethyl phthalate, di-n-butyl phthalate, diisobutyl phthalate and the like. Preferable are unsaturated aliphatic carboxylates such as methacrylates and the like and phthalates such as maleates and

the like, and further preferable are phthalate diesters.

(0054)

(a-4) Organomagnesium compound

As the magnesium compound used for synthesis of a solid catalyst component (a), for example, magnesium compounds having a magnesium-carbon bond or magnesium-hydrogen bond and having a reducing ability, and magnesium compounds having no reducing ability and the like are listed. Specific examples of the magnesium compound having a reducing ability include dialkylmagnesium compounds such as dimethylmagnesium, diethylmagnesium, dibutylmagnesium, butylethylmagnesium and the like, alkylmagnesium halide compounds such as butylmagnesium chloride and the like, alkylalkoxymagnesium compounds such as butylethoxymagnesium and the like and alkylmagnesium hydrides such as butylmagnesium hydride and the like. These magnesium compounds having a reducing ability may also be used in the form of a complex compound with an organoaluminum compound.

(0055)

On the other hand, specific examples of the magnesium compound having no reducing ability include magnesium dihalide compounds such as magnesium dichloride and the like, alkoxymagnesium halide compounds such as methoxymagnesium chloride, ethoxymagnesium chloride, butoxymagnesium chloride and the like, dialkoxymagnesium compounds such as

diethoxymagnesium, dibutoxymagnesium and the like and salts of carboxylic acids such as magnesium laurate, magnesium stearate and the like. These magnesium compounds having no reducing ability may also be compounds synthesized from magnesium compounds having a reducing ability by a known method, previously or in preparing a solid catalyst component (a).

(0056)

(a-5) Ether compound

As the ether compound used for synthesis of a solid catalyst component (a), for example, dialkylethers such as diethylether, dibutyl ether, diisobutyl ether, diamylether, diisoamylether, methyl butyl ether, methyl isoamyl ether, ethyl isobutyl ether and the like, are listed. Preferable are dibutyl ether and diisoamyl ether.

(0057)

(a-6) Organic acid halide compound

As the organic acid halide compound used for synthesis of a solid catalyst component (a), mono and polyvalent carboxylic halides are listed, and aliphatic carboxylic halides, alicyclic carboxylic halides, aromatic carboxylic halides and the like are exemplified. Specific examples thereof include acetyl chloride, propionic chloride, butyric chloride, valeric chloride, acrylic chloride, methacrylic chloride, benzoyl chloride, toluic chloride, anisic chloride, succinic chloride, phthalic chloride and the like. Preferable are aromatic

carboxylic chlorides such as benzoyl chloride, toluic chloride, phthalic chloride and the like, and further preferable is phthalic chloride.

(0058)

#### Synthesis of solid catalyst component

As the method of producing a solid catalyst component (a), for example, the following methods are mentioned.

(1) A magnesium compound in the form of liquid, or a complex compound composed of a magnesium compound and an electron donor is reacted with a deposition agent, then, the reaction product is treated with a titanium compound, or a titanium compound and electron donor.

(2) A magnesium compound in the form of solid, or a complex compound composed of a magnesium compound in the form of solid and an electron donor is treated with a titanium compound, or a titanium compound and electron donor.

(3) A method of reacting a magnesium compound in the form of liquid and a titanium compound in the form of liquid in the presence of an electron donor, to precipitate a titanium complex in the form of solid.

(4) The reaction product obtained in (1), (2) or (3) is further treated with a titanium compound, or an electron donor and titanium compound.

(5) A method of reducing an alkoxytitanium compound by an organomagnesium compound such as a Grignard's reagent and

the like in the co-presence of an organosilicon compound having a Si-O bond to obtain a solid product which is treated with an ester compound, ether compound and  $TiCl_4$ .

(6) A method of reducing a titanium compound by an organomagnesium compound in the presence of an organosilicon compound or of an organosilicon compound and ester compound, to obtain a solid product which is treated with a mixture of an ether compound and titanium tetrachloride, then, with an organic acidhalide compound, added in this order, then, treating the treated solid with a mixture of an ether compound and titanium tetrachloride, or a mixture of an ether compound, titanium tetrachloride and ester compound.

(7) A method of contacting a catalytic reaction product of a metal oxide, dihydrocarbylmagnesium and halogen-containing alcohol with an electron donor and titanium compound, after treating the catalytic reaction product with a halogenating agent or without such treatment.

(8) A method of contacting a magnesium compound such as a magnesium salt of an organic acid, alkoxy-magnesium and the like with an electron donor and titanium compound, after treating the magnesium compound with a halogenating agent or without such treatment.

(9) A method of treating the compound obtained in (1) to (8) with any of halogens, halogen compounds and aromatic hydrocarbons.

Of these methods of synthesizing a solid catalyst, preferable are methods (1) to (6), and further preferable is a method (6). These synthesis reactions are usually conducted all in an inert gas atmosphere such as nitrogen, argon and the like.

(0059)

It is preferable that titanium compounds, organosilicon compounds and ester compounds are dissolved or diluted in a suitable solvent before use. As this solvent, for example, aliphatic hydrocarbons such as hexane, heptane, octane, decane and the like, aromatic hydrocarbons such as toluene, xylene and the like, alicyclic hydrocarbons such as cyclohexane, methylcyclohexane, decalin and the like, ether compounds such as diethyl ether, dibutyl ether, diisoamyl ether, tetrahydrofuran and the like.

(0060)

The temperature for a reduction reaction using an organomagnesium compound is usually from -50 to 70°C, preferably from -30 to 50°C, particularly preferably from -25 to 35°C. When the reduction reaction temperature is too high, catalyst activity may lower. The dropping time of an organomagnesium compound is not particularly restricted, and usually from about 30 minutes to 12 hours. Further, after completion of the reduction reaction, a post reaction may also be conducted at temperatures from 20 to 120°C.

(0061)

Furthermore, it is also possible that, in effecting a reduction reaction, porous substances such as an inorganic oxide, organic polymer and the like are allowed to exist, and a solid product is impregnated in the porous substance. This porous substance is preferably a substance having a fine pore volume when the fine pore diameter is from 20 to 200 nm of 0.3 ml/g or more and having an average particle size of 5 to 300  $\mu$ m.

(0062)

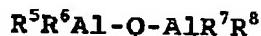
As the porous inorganic oxide,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$  and combined oxides thereof are listed. As the porous polymer, for example, polystyrene-based porous polymers such as polystyrene, styrene-divinylbenzene copolymer and the like, polyacrylate-based porous polymers such as ethyl polyacrylate, methyl acrylate-divinylbenzene copolymer, methyl polymethacrylate, methyl methacrylate-divinylbenzene copolymer and the like, and polyolefin-based porous polymers such as polyethylene, ethylene-methyl acrylate copolymer, polypropylene and the like, are listed. Of these porous substances, preferable are  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and styrene-divinylbenzene copolymer.

(0063)

(b) Organoaluminum compound

The organoaluminum compound (b), catalyst system used

in production of a propylene-ethylene block copolymer (i) and a propylene polymer (ii) used in a mixture (iii) in the present invention, has at least one Al-carbon bond in the molecule, and typical examples thereof are represented by the following general formula:



(wherein,  $R^4$  to  $R^8$  represent a hydrocarbon group having 1 to 8 carbon atoms, Y represents a halogen atom, hydrogen or alkoxy group.  $R^4$  to  $R^8$  may be the same or different. m represent a number satisfying  $2 \leq m \leq 3$ .). Specific examples of the organoaluminum compound include trialkylaluminums such as triethylaluminum triisobutylaluminum and the like, dialkylaluminum hydride such as diethylaluminum hydride, diisobutylaluminum hydride and the like, dialkylaluminum halides diethylaluminum chloride, diisobutylaluminum chloride and the like, mixtures of trialkylaluminums and dialkylaluminum halides such as a mixture of triethylaluminum and diethylaluminum chloride, alkylalumoxanes such as tetraethyldialumoxane, tetrabutyldialumoxane and the like, and other aluminum compounds.

(0064)

Of these organoaluminum compounds, trialkylaluminums, mixtures of trialkylaluminums and dialkylaluminum halides, and alkylalumoxanes are preferable, and triethylaluminum,

tiriisobutylaluminum, a mixture of triethylaluminum and diethylaluminum chloride are further preferable, or tetraethyldialumoxane is preferable.

(0065)

(c) Electron donor

As the electron donor (b), catalyst system used in production of a propylene-ethylene block copolymer (i) and a propylene polymer (ii) used in a mixture (iii) in the present invention, there are listed those generally used such as oxygen-containing electron donors such as alcohols, phenols, ketones, aldehydes, carboxylic acids, organic or inorganic esters, ethers, acid amides, acid anhydrides and the like, and nitrogen-containing electron donors such as ammonias, amines, nitriles, isocyanates and the like. Of these electron donors, preferable are esters of inorganic acids and ethers.

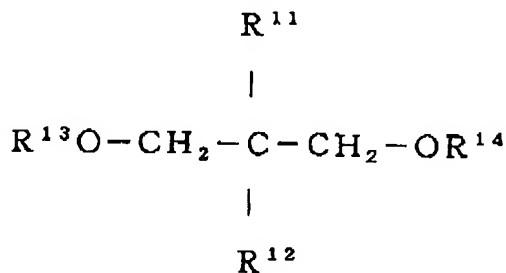
(0066)

The esters of inorganic acids are preferably silicon compounds of the general formula  $R^9_nSi(OR^{10})_{4-n}$  (wherein,  $R^9$  represents a hydrocarbon group having 1 to 20 carbon atoms or a hydrogen atom,  $R^{10}$  represents a hydrocarbon group having 1 to 20 carbon atoms,  $R^9$  and  $R^{10}$  each may have different substituents in the same molecule, and  $n$  represents a number satisfying  $0 \leq n < 4$ ). Specific examples thereof include tetrabutoxysilane, butyltrimethoxysilane, tert-butyl-n-propyldimethoxysilane, dicyclopentyldimethoxysilane,

cyclohexylethyldimethoxysilane and the like.

(0067)

Further, as the ethers, dialkyl ethers and diether compounds of the general formula:



(wherein,  $R^{11}$  to  $R^{14}$  represent a linear or branched alkyl group having 1 to 20 carbon atoms, an alicyclic hydrocarbon group, an aryl group or an aralkyl group, and  $R^{11}$  or  $R^{12}$  may be a hydrogen atom.) are listed. Specific examples thereof include dibutyl ether, diamyl ether, 2,2-diisobutyl-1,3-dimethoxypropane, 2,2-dicyclopentyl-1,3-dimethoxypropane and the like.

(0068)

Of these electron donor components, organosilicon compounds of the general formula  $R^{15}R^{16}Si(OR^{17})_2$  are particularly preferably used. In the formula,  $R^{15}$  is a hydrocarbon group having 3 to 20 carbon atoms of which carbon atom adjacent to Si is secondary or tertiary, and specific examples thereof include branched alkyl groups such as an isopropenyl group, sec-butyl group, tert-butyl group, tert-amyl group and the like, cycloalkyl groups such as a cyclopentyl group, cyclohexyl group

and the like, cycloalkenyl groups such as a cyclopentenyl group and the like, aryl groups such as a phenyl group, tolyl group and the like. Further, in the formula, R<sup>16</sup> is a hydrocarbon group having 1 to 20 carbon atoms, and specific examples thereof include linear alkyl groups such as a methyl group, ethyl group, propyl group, butyl group, pentyl group and the like, branched alkyl groups such as an isopropenyl group, sec-butyl group, tert-butyl group, tert-amyl group and the like, cycloalkyl groups such as a cyclopentyl group, cyclohexyl group and the like, cycloalkenyl groups such as a cyclopentenyl group and the like, aryl groups such as phenyl group, tolyl group and the like, and other hydrocarbon groups. In the formula, R<sup>17</sup> represents a hydrocarbon group having 1 to 20 carbon atoms, preferably a hydrocarbon group having 1 to 3 carbon atoms. Specific examples of the organosilicon compound used as such an electron donor component include  
tert-butyl-n-propyldimethoxysilane,  
dicyclopentyldimethoxysilane,  
cyclohexylethyldimethoxysilane and the like.

(0069)

## (2) Polymerization method

As the method of polymerizing a propylene-based polymer of the present invention, bulk polymerization, solution polymerization, slurry polymerization and gas phase polymerization are listed. The bulk polymerization is a method

of conducting polymerization using a liquid olefin as a medium at polymerization temperature, the solution polymerization or slurry polymerization is a method of conducting polymerization in an inert hydrocarbon solvent such as propane, butane, isobutene, pentane, hexane, heptane, octane and the like, and the gas phase polymerization is a method in which a monomer in the form of gas is used as a medium and a monomer in the form of gas is polymerized in this medium. These polymerization methods may be conducted by any of batch-wise mode and continuous mode, and these polymerization methods may be effected in any combination. As the more specific production method, there are a polymerization method in which, in the presence of a catalyst system composed of the above-mentioned solid catalyst component (a), organoaluminum compound (b) and electron donor component (c), at least three polymerization chambers are placed in series, and after polymerization of the component (A), the product is transferred to the next polymerization chamber, then, the component (B) is polymerized in this polymerization chamber, then, the component (c) is continuously polymerized in the next polymerization chamber, and other methods. From the industrial and economical standpoint, a gas phase polymerization method of continuous mode is preferable.

(0070)

The use amount of the organoaluminum compound (b) is from 1 to 1000 mol, preferably from 5 to 600 mol per mol of titanium

atom contained in the solid catalyst component (a).

(0071)

The use amount of the electron donor component (c) is from 0.1 to 2000 mol, preferably from 0.3 to 1000 mol, further preferably from 0.5 to 800 mol per mol of a titanium atom contained in the solid catalyst component (a), and from 0.001 to 5 mol, preferably from 0.005 to 3 mol, further preferably from 0.01 to 1 mol per mol of an aluminum atom contained in the organoaluminum compound (b).

(0072)

The polymerization can be conducted at temperatures from -300 to 300°C, and the polymerization temperature is preferably from 20 to 180°C. The polymerization pressure is not particularly restricted, and from industrial and economical standpoint, generally from normal pressure to 10 MPa, preferably from 0.2 to 5 MPa.

(0073)

As the molecular weight controlling agent, hydrogen is preferable. The feeding amount of water can be appropriately determined depending on the application of the polypropylene-based resin composition of the present invention.

(0074)

The method of feeding catalyst components to a polymerization chamber is not particularly restricted except

that feeding is effected under condition of no water in an inert gas such as nitrogen, argon and the like. The solid catalyst component (a), organoaluminum compound (b) and electron donor component (c) may be separately fed, or any two of them or all of them are previously allowed to contact each other before feeding.

(0075)

In the production of a propylene-based polymer of the present invention, the following preliminary polymerization may be conducted before effecting polymerization (main polymerization).

As the method of preliminary polymerization, known methods are mentioned, and there is exemplified a method in which, in the presence of a solid catalyst component (a) and an organoaluminum compound (b), polymerization is conducted in slurry condition using a solvent while feeding a small amount of propylene. As the solvent used in the preliminary polymerization, inert hydrocarbons such as propane, butane, isobutene, pentane, isopentane, hexane, heptane, octane, cyclohexane, benzene and toluene, and propylene in the form of liquid are mentioned, two or more of them may be mixed and used.

(0076)

The used amount of the organoaluminum compound (b) in the preliminary polymerization is from 0.5 to 700 mol, preferably

from 0.8 to 500 mol, further preferably from 1 to 200 per mol of a titanium atom contained in the solid catalyst component (a).

(0077)

The amount of propylene to be subjected to the preliminary polymerization is from 0.01 to 1000 g, preferably from 0.05 to 500 g, further preferably from 0.1 to 200 g per 1 g of a solid catalyst component.

(0078)

The slurry concentration in the preliminary polymerization is preferably from 1 to 500 g/L, further preferably from 3 to 300 g/L in terms of the weight of a solid catalyst component (a) contained per liter of a solvent. The previously polymerization temperature is preferably from -20 to 100°C, further preferably from 0 to 80°C. The partial pressure of propylene in a gas phase portion during the preliminary polymerization is preferably from 0.001 to 2.0 Mpa, further preferably from 0.01 to 1.0 Mpa, however, this is not applied to propylene which is in the form of liquid under pressure and temperature for the preliminary polymerization. Further, the preliminary polymerization time is not particularly restricted, and usually, it is suitably from 2 minutes to 15 hours.

(0079)

As the method of feeding a solid catalyst component (a), organoaluminum compound (b) and propylene in the preliminary

polymerization, there are listed a method in which a solid catalyst component (a) and an organoaluminum compound (b) are allowed to contact, then, propylene is fed to this, a method in which a solid catalyst component (a) and propylene are allowed to contact, then, an organoaluminum compound (b) is fed, and other methods. As the method of feeding propylene, there are a method in which propylene is sequentially fed while keeping the pressure in a polymerization chamber at a given level, a method in which all of propylene of given amount is fed first, and other methods. Further, for controlling the molecular weight of the resulting prepolymer, a chain transfer agent such as hydrogen and the like may be added.

(0080)

Further, in the preliminary polymerization, an electron donor component (c) may be allowed to co-exist, if necessary. The use amount is from 0.01 to 400 mol, preferably from 0.02 to 200 mol, further preferably from 0.03 to 100 mol per mol of a titanium atom contained in the solid catalyst component (a), and from 0.003 to 5 mol, preferably from 0.005 to 3 mol, further preferably from 0.01 to 2 mol per mol of an aluminum atom contained in the organoaluminum compound (b).

(0081)

The method of feeding the electron donor component used in the preliminary polymerization is not particularly restricted, and a solid catalyst component (a) and an

organoaluminum compound (b) may be separately fed, or may be previously allowed to contact before feeding. The propylene used in the preliminary polymerization may be the same as or different from propylene used in the main polymerization.

(0082)

Explanation of a method (II) of obtaining a polypropylene-based resin composition by melt-blending a propylene-based polymer partially having a propylene polymer component (B) and a propylene-ethylene random copolymer component (C)

The above-mentioned method (II) is not particularly restricted, and preferable is a method in which 98.7 to 86% by weight of a polypropylene-based resin (D) is mixed with 1.3 to 14% by weight of a propylene-based polymer composition (E) composed of 40 to 70% by weight of a propylene-based polymer component (A1) and 60 to 30% by weight of a propylene polymer component (B). Regarding the compounding ratio of the polypropylene-based resin (D) to the propylene-based polymer composition (E), more preferably, the amount of the polypropylene-based resin (D) is 98 to 88% by weight, and the amount of the propylene-based polymer composition (E) is 2 to 12% by weight.

(0083)

As the propylene-based polymer component (A1) and the propylene polymer component (B) used in the propylene-based

polymer composition (E), those listed above are mentioned.

(0084)

Regarding the compounding ratio of the propylene-based polymer component (A1) and the propylene polymer component (B) used in the propylene-based polymer composition (E), the amount of the propylene-based polymer component (A1) is preferably from 40 to 70% by weight (namely, the amount of the propylene polymer component (B) is from 60 to 30% by weight), more preferably, the amount of the propylene-based polymer component (A1) is from 45 to 65% by weight (namely, the amount of the propylene polymer component (B) is from 55 to 35% by weight), from the standpoint of dispersibility of the propylene-based polymer component (A1).

(0085)

The method of producing a propylene-based polymer composition (E) is not particularly restricted, and preferably, there are mentioned production methods using the same catalyst systems and polymerization methods as shown in the method (I) of obtaining a polypropylene-based resin composition as a propylene-based polymer having the above-mentioned propylene-based polymer component (A1), propylene polymer component (B) and propylene-ethylene random copolymer component (C).

(0086)

More specifically, there is exemplified a method in which,

in the presence of a catalyst system composed of the above-mentioned solid catalyst component (a), organoaluminum compound (b) and electron donor component (c), at least two polymerization chambers are placed in series, and after polymerization of the component (A1), the product is transferred to the next polymerization chamber, and the propylene polymerization component (B) is continuously polymerized, and other methods.

(0087)

As the method of mixing a polypropylene-based resin (D) and a propylene-based polymer composition (E), there are exemplified methods using kneading machines such as a single-screw extruder, twin-screw extruder, Banbury mixer, heat roll and the like. More specifically, the following methods are mentioned.

(1) A method in which a polymerization powder of a polypropylene-based resin (D) and a polymerization powder of a propylene-based polymer composition (E) are kneaded using the above-mentioned kneading machine.

(2) A method in which a polymerization powder of a polypropylene-based resin (D) and a polymerization powder of a propylene-based polymer composition (E) are separately individually kneaded using a single-screw extruder or twin-screw extruder to produce pellets, thereafter, the pellet of the polypropylene-based resin (D) and the pellet of the

propylene-based polymer (E) are kneaded using a single-screw extruder or twin-screw extruder.

(3) A propylene-based polymer composition (E) previously pelletized using a single-screw extruder or twin-screw extruder is added to a kneading machine using a quantitative feeder and kneaded in a process of pelletizing a polymerization powder of a polypropylene-based resin (D).

Preferably, in the method (2) or (3), a propylene-based polymer composition (E) previously kneaded using a single-screw extruder or twin-screw extruder is used.

(0088)

If necessary, a screen pack may be mounted on a dice of a single-screw extruder or twin-screw extruder. The screen pack to be mounted is preferably a metal fiber-sintered filter, and described, for example, in "Kikai Sekkei (1931, March, Vol. 25, No. 3, pp. 109 to 113)" .

The kneading temperature is usually from 170 to 250°C, preferably from 190 to 240°C.

(0089)

The polypropylene-based resin composition of the present invention is more preferably a polypropylene-based resin composition comprising 35 to 88% by weight of a polypropylene-based resin composition composed of a propylene-based polymer component (A1) and a propylene-based polymer component (A2), 0 to 20% by weight of a propylene

homopolymer (F), 10 to 35% by weight of an elastomer (G) and 2 to 30% by weight of an inorganic filler (H).

(0090)

The propylene homopolymer (F) used in the present invention is a propylene homopolymer obtained by homopolymerizing propylene.

(0091)

The elastomer (G) used in the present invention is not particularly restricted, and preferably an elastomer containing a rubber component, and there are exemplified vinyl aromatic compound-containing rubber, ethylene-propylene random copolymer rubber, ethylene- $\alpha$ -olefin random copolymer rubber and elastomer composed of a mixture of them, and the like.

(0092)

As vinyl aromatic compound-containing rubber used in the elastomer (G), for example, a block copolymer composed of a vinyl aromatic compound polymer block and a conjugated diene-based polymer block, and the like are listed, and the hydrogen addition ratio of double bonds at the conjugated diene portion is preferably 80% or more, more preferably 85% or more.

(0093)

The molecular weight distribution (Q value) of the above-mentioned vinyl aromatic compound-containing rubber according to a GPC (gel permeation chromatography) method is

preferably 2.5 or less, more preferably 2.3 or 1 ss.

(0094)

The average content of vinyl aromatic compounds contained in the above-mentioned vinyl aromatic compound-containing rubber is preferably from 10 to 20% by weight, more preferably from 12 to 19% by weight.

(0095)

The melt flow rate (MFR, JIS-K-6758, 230°C) of the above-mentioned vinyl aromatic compound-containing rubber is preferably from 1 to 15 g/10 minutes, more preferably from 2 to 13 g/10 minutes.

(0096)

Examples of the vinyl aromatic compound-containing rubber include block copolymers such as styrene-ethylene-butene-styrene-based rubber (SEBS), styrene-ethylene-propylene-styrene-based rubber (SEPS), styrene-butadiene-based rubber (SBR), styrene-butadiene-styrene-based rubber (SBS), styrene-isoprene-styrene-based rubber (SIS) and the like, and block copolymers obtained by hydrogenating these rubber components. Further, rubbers obtained by reacting a vinyl aromatic compound such as styrene and the like with ethylene-propylene-non-conjugated diene-based rubber (EPDM) are also listed. Still further, two or more vinyl aromatic compound-containing rubbers may also be used.

(0097)

The method of producing the above-mentioned vinyl aromatic compound-containing rubber is not particularly restricted, and for example, a method in which a vinyl aromatic compound is bonded to olefin-based copolymer rubber or conjugated diene rubber by polymerization, reaction and the like, and other methods are mentioned.

(0098)

The ethylene-propylene random copolymer rubber used in an elastomer (G) is random copolymer rubber of ethylene and propylene, and the molecular weight distribution (Q value) of the ethylene-propylene random copolymer rubber according to a GPC (gel permeation chromatography) method is preferably 2.7 or less, more preferably 2.5 or less.

(0099)

The content of propylene contained in the above-mentioned ethylene-propylene random copolymer rubber is preferably from 20 to 30% by weight, more preferably from 22 to 28% by weight.

(0100)

The melt flow rate (MFR, JIS-K-6758, 190°C) of the above-mentioned ethylene-propylene random copolymer rubber is preferably from 1 to 15 g/10 minutes, more preferably from 2 to 13 g/10 minutes.

(0101)

The ethylene- $\alpha$ -olefin random copolymer rubber used in

a elastomer (G) is not particularly restricted, and random copolymer rubbers composed of ethylene and an  $\alpha$ -olefin may be permissible. This  $\alpha$ -olefin is an  $\alpha$ -olefin having 4 to 12 carbon atoms, and for example, butene-1, pentene-1, hexene-1, heptene-1, octene-1, decene and the like are listed, and preferable are butene-1, hexene-1 and octene-1.

(0102)

As the ethylene- $\alpha$ -olefin random copolymer rubber, for example, ethylene-butene-1 random copolymer rubber, ethylene-hexene-1 random copolymer rubber, ethylene-octene-1 random copolymer rubber and the like are listed, and preferable is ethylene-octene-1 random copolymer rubber or ethylene-butene-1 random copolymer rubber. Further, two or more ethylene- $\alpha$ -olefin random copolymer rubbers may also be used.

(0103)

The ethylene-octene-1 random copolymer rubber used in an elastomer (G) is random copolymer rubber of ethylene and octene-1, and the molecular weight distribution (Q value) of the ethylene-octene-1 random copolymer rubber according to a GPC (gel permeation chromatography) method is preferably 2.5 or less, more preferably 2.3 or less.

(0104)

The content of octene-1 contained in the above-mentioned ethylene-octene-1 random copolymer rubber is preferably from

15 to 45% by weight, more preferably from 18 to 42% by weight.

(0105)

The melt flow rate (MFR, JIS-K-6758, 190°C) of the above-mentioned ethylene-octene-1 random copolymer rubber is preferably from 1 to 15 g/10 minutes, more preferably from 2 to 13 g/10 minutes.

(0106)

The ethylene-butene-1 random copolymer rubber used in a elastomer (G) is random copolymer rubber of ethylene and butene-1, and the Q value of the ethylene-butene-1 random copolymer rubber according to a GPC method is preferably 2.7 or less, more preferably 2.5 or less.

(0107)

The content of butene-1 contained in the above-mentioned ethylene-butene-1 random copolymer rubber is preferably from 15 to 35% by weight, more preferably from 17 to 3% by weight.

(0108)

The melt flow rate (MFR, JIS-K-6758, 190°C) of the above-mentioned ethylene-butene-1 random copolymer rubber is preferably from 1 to 15 g/10 minutes, more preferably from 2 to 13 g/10 minutes.

(0109)

The method of producing the above-mentioned ethylene-propylene random copolymer rubber and ethylene- $\alpha$ -olefin random copolymer rubber is not particularly restricted,

and they can be produced by copolymerizing ethylene and propylene, or ethylene and various  $\alpha$ -olefins using a known catalyst by a known polymerization method. As the known catalyst, for example, catalyst systems composed of a vanadium compound and an organoaluminum compound, Ziegler Natta catalyst systems and metallocene catalyst systems and the like are listed, and as the known polymerization method, a solution polymerization method, slurry polymerization method, high pressure ion polymerization method and gas phase polymerization method and the like are listed.

(0110)

The inorganic filler (H) used in the present invention is not particularly restricted, and used usually for improving rigidity, and examples thereof include calcium carbonate, barium sulfate, mica, crystalline calcium silicate, talc, magnesium sulfate fiber and the like, and preferable are talc and magnesium sulfate fiber. These inorganic filler may be used in combination of two or more.

(0111)

The talc used in an inorganic filler (H) is not particularly restricted, and preferably which obtained by grinding water-containing magnesium silicate. The crystal structure of the molecule of water-containing magnesium silicate is a pyrophyllite type three-layer structure, and talc is formed by lamination of this structure. Talc is particularly

preferably in the form of flat plate obtained by finely grinding a crystal of the molecule of water-containing magnesium silicate to about unit layer.

(0112)

The above-mentioned talc has an average particle size of preferably 3  $\mu\text{m}$  or less. Here, the average particle size of talc means 50% equivalent particle size  $D_{50}$  obtained from an integral distribution curve of a minus mesh method measured by suspending the talc in a dispersion medium such as water, alcohol and the like, using a centrifugal precipitation type particle size distribution measuring apparatus.

(0113)

The above-mentioned talc may be used without treatment, alternatively, for improving dispersibility and boundary adhesion with a polypropylene-based resin composition composed of a propylene-based polymer component (A1) and a propylene-based polymer component (A2), the surface thereof may be treated with known various silane coupling agent, titanium coupling agents, higher fatty acids, higher fatty esters, higher fatty amides, higher fatty salts or other surfactants.

(0114)

The magnesium sulfate fiber used in an inorganic filler (H) is not particularly restricted, and the average fiber length of the magnesium sulfate fiber is preferably from 5 to 50  $\mu\text{m}$ , further preferably from 10 to 30  $\mu\text{m}$ . Further, the average

fiber diameter of the magnesium sulfate fiber is preferably from 0.3 to 2  $\mu\text{m}$ , further preferably from 0.5 to 1  $\mu\text{m}$ .  
(0115)

To the polypropylene-based resin composition of the present invention, various additives may be added in an amount causing no deterioration in the object and effect thereof. Examples of the additive include antioxidants, ultraviolet absorbers, lubricants, pigments, antistatic agents, copper inhibitors, flamer retardants, neutralizing agent, foaming agents, plasticizers, nucleating agents, de-foaming agents, cross-linking agents and the like. For improving heat resistance, weather resistance and anti-oxidation stability, it is preferable to add an antioxidant or ultraviolet absorber.  
(0116)

These additives, the above-mentioned elastomer (G) and the above-mentioned inorganic filler (H) may be compounded with a pellet of a polypropylene-based resin composition previously melt-kneaded, or compounded in a stage of palletizing a polypropylene-based resin composition.

(0117)

The polypropylene-based resin composition of the present invention can be molded into an injection molded body by a known injection molding method. The use of an injection molded body is particularly preferably an injection molded body for automobile, and examples thereof include a door trim, pillar,

instrumental panel, bumper and the like.

(0118)

[EXAMPLES]

The following examples and comparative examples will illustrate the present invention below, but do not limit the scope of the invention.

The physical properties of polymers and compositions used in the examples and comparative examples were measured according to the following methods.

(0119)

(1) Limiting viscosity (unit: dl/g)

Reduction viscosities were measured at three points of concentration of 0.1, 0.2 and 0.5 g/dl, using a Ubbelohde viscometer. The limiting viscosity was obtained by a calculation method described in page 491 of "Kobunshi Yoeki, Kobunshi Jikkengaku 11 (1982, published by Kyoritsu Shuppan K.K.)", namely, by an extrapolation method in which reduction viscosities are plotted against concentration and the concentration is extrapolated into zero. It was measured at a temperature of 135°C, using tetralin as a solvent.

(0120)

(1-1) Limiting viscosity of propylene-ethylene block polymer

(i)

(1-1a) Limiting viscosity of propylene homopolymerization portion (first segment of copolymer (i)):  $[\eta]_p$

Regarding the  $[\eta]_p$  of a propylene homopolymerization portion, first segment of a propylene-ethylene block copolymer (i), a propylene homopolymer was removed out of a polymerization chamber after a first process, polymerization of a propylene homopolymer, in production thereof, and the  $[\eta]_p$  of the removed propylene homopolymer was measured.

(0121)

(1-1b) Limiting viscosity:  $[\eta]_{sp}$  of propylene-ethylene random copolymer portion (second segment of copolymer (i))

Regarding the limiting viscosity:  $[\eta]_{sp}$  of a propylene-ethylene random copolymer portion, second segment of a propylene-ethylene block copolymer (i), the limiting viscosity:  $[\eta]_p$  of a propylene homopolymer portion and the limiting viscosity:  $[\eta]_p$  of the whole propylene-ethylene block copolymer were measured respectively, and the weight ratio: X of a propylene-ethylene random copolymer portion to the whole propylene-ethylene block copolymer was used, and  $[\eta]_{sp}$  was calculated according to the following formulae (weight ratio: X to the whole propylene-ethylene block copolymer was obtained by the following measuring method (2)).

$$[\eta]_{sp} = [\eta]_p/X - (1/X - 1)[\eta]_p$$

$[\eta]_p$  : Limiting viscosity (dl/g) of propylene homopolymer portion

$[\eta]_p$  : Limiting viscosity (dl/g) of the whole propylene-ethylene block copolymer

(0122)

(1-2) Limiting viscosity:  $[\eta]_p$  of propylene homopolymer

The limiting viscosity:  $[\eta]_p$  of the propylene homopolymer used in a mixture (iii) was measured according to the above-mentioned method (1) using a propylene homopolymer.

(0123)

(1-3) Limiting viscosity:  $[\eta]_1$ ,  $[\eta]_2$  of propylene-based polymer component (A1)

In the case of one-stage polymerization, the limiting viscosity was measured according to the above-mentioned method (1) ( $[\eta]_1$ ). In the case of two-stage polymerization, a sample extracted from a polymerization chamber after the one-stage polymerization process and a final sample after the two-stage polymerization process were subjected to the above-mentioned measuring method (1) ( $[\eta]_1$ ,  $[\eta]_2$ ). The limiting viscosity  $[\eta]_2$  of a component polymerized in the second step was calculated according to the following formulae.

$$[\eta]_2 = ([\eta]_T - [\eta]_1 \times X_1) / X_2$$

$[\eta]_T$  : Limiting viscosity (dl/g) of final sample after two-stage polymerization process

$[\eta]_1$  : Limiting viscosity (dl/g) of sample extracted from polymerization chamber after one-stage polymerization process

$X_1$ : weight ratio of component polymerization in first step

$X_2$ : weight ratio of component polymerization in second

step

$X_1$  and  $X_2$  were calculated from material balance in polymerization.

(0124)

The weight ratio: X of a propylene-ethylene random copolymer portion to the whole propylene-ethylene block copolymer and the ethylene content:  $(C_2')_{EP}$  of a propylene-ethylene random copolymer portion in a propylene-ethylene block copolymer were determined based on the report of Kakugo et al. (Macromolecules 1982, 15, 1150-1152) from a  $^{13}\text{C}$ -NMR spectrum measured according to the following conditions.

About 200 mg of a propylene-ethylene block copolymer was uniformly dissolved in 3 ml of orthodichlorobenzene to prepare a sample in a 10 mmφ test tube, and the  $^{13}\text{C}$ -NMR spectrum of this sample was measured according to the following conditions.

Measuring temperature: 135°C

Pulse repeating time: 10 seconds

Pulse width: 45°

Accumulated frequency: 2500

(0125)

(3) Isotactic pentad fraction

The isotactic pentad fraction means a fraction of propylene monomer units situated at the isotactic chain in pentad unit in a polypropylene molecule chain, in other words, at the

center of a chain of five continuous meso bonding of propylene monomer units, measured by a method published in A. Zambelli et al. Macromolecules, 6, 925 (1973), namely, by using  $^{13}\text{C}$ -NMR. The assignment of the NMR absorption peak was conducted based in Macromolecules, 8, 687 (1975) published thereafter.

(0126)

Specifically, the isotactic pentad fraction was measured as an area fraction of mmmm peaks in all absorption peaks in a methyl carbon region of the  $^{13}\text{C}$ -NMR spectrum. By this method, the isotactic pentad of an NPL standard substance CRM No. M19-14 Polypropylene PP/MWD/2 of U.K. NATIONAL PHYSICAL LABORATORY was measured, to find it was 0.944.

(0127)

(4) Comonomer content of propylene-based polymer component  
(A1)(unit: wt%)

It was determined by measuring by an infrared spectrometry according to a method described in Polymer Handbook (1995, published by Kinokuniya Shoten), p. 616 and following pages.

(0128)

(5) Molecular weight distribution (Q value,  $M_w/M_n$ )

It was measured by G.P.C. (gel permeation chromatography) under the following conditions.

Type: 150 CV type (Millipore Waters)

Column: Shodex M/S 80

Measuring temperature: 145°C

Solvent: orthodichlorobenzene

Sample concentration: 5 mg/8 mL

A calibration curve was made using standard polystyrene.

Mw/Mn of standard polystyrene (NBS706: Mw/Mn=2.0) measured under this condition was from 1.9 to 2.0.

(0129)

(6) Melting temperature peak ( $T_m$ , unit: °C)

Using a differential scanning calorimeter (DSC-7, manufactured by Perkin Elmer), a polymer was heat-treated at 220°C for 5 minutes, then, cooled down to 150°C at a temperature decreasing rate of 300°C/min and kept at 150°C for 1 minute, further cooled down to 50°C at a temperature decreasing rate of 5°C/min and kept at 50°C for 1 minute, further, heated from 50°C to 180°C at a temperature increasing rte of 5°C/min, and the melting peak temperature in this operation was measured as  $T_m$ .

(0130)

(7) Melt flow rate (MFR, unit: g/10 minutes)

It was measured according to a method defined in JIS-K-6758. Unless otherwise stated, measurement was conducted at a measuring temperature of 230°C and a load of 2.16 kg.

(0131)

(8) Die swell (D. S.)

It was measured using Capillograph 1B manufactured by Toyo Seiki Seisakusho K.K. under the following conditions.

Measuring temperature: 220°C

L/D: 40

Shearing speed:  $2.432 \times 10^3$  sec<sup>-1</sup>

(0132)

(9) Number of granular structure -1 (unit: number/10 cm<sup>2</sup>)

A film processed under the following conditions using a T die extruder was subjected to quantitative analysis according to the following method using an image analysis apparatus.

Film processing conditions:

A film having a width of 50 mm and a thickness of 50 μm was produced by an extruder V-20 manufactured by Tanabe Plastic Kikai K.K. and a film drawing apparatus.

Quantitative analysis method

Images (900 dpi, 8 bit) of a film were incorporated into a computer by a scanner GT-9600 manufactured by EPSON, and the images were binarized by an image analysis soft, A zo kun manufactured by Asahi Engineering. Granular structures were recognized as clearer places than surrounding places. Since the forms of granular structures are not regular, the diameter of a circle having the same area as that of a granular structure was recognized as the size of the granular structure, and the number of granular structures having a diameter of 200 μm or more per 10 cm<sup>2</sup> of a film was counted.

(0133)

(10) Number of granular structure-2 (unit: number/43 cm<sup>2</sup>)

A film was manufactured by the same manner as in the above-mentioned item (9) and analyzed by the following method

**Quantitative analysis method**

Images (200 dpi, 8 bit) of a film were incorporated into a computer by a scanner GT-9600 manufactured by EPSON, and the images were binarized by an image analysis soft, A zo kun manufactured by Asahi Engineering. Granular structures were recognized as clearer places than surrounding places. Since the forms of granular structures are not regular, the diameter of a circle having the same area as that of a granular structure was recognized as the size of the granular structure, and the number of granular structures having a diameter of 200  $\mu\text{m}$  or more per 43  $\text{cm}^2$  of a film was counted.

(0134)

**(11) Tensile test (Ultimate Elongation, unit: %)**

It was measured by a method defined in ASTM D638. Measurement was conducted using a specimen having a thickness of 3.2 mm molded by injection molding. The tensile speed was 10 mm/min, 50 mm/min or 70 mm/min, and the ultimate elongation (UE) was evaluated.

(0135)

**(12) Flexural modulus (FM, unit: kg/cm<sup>2</sup>)**

It was measured according to a method defined in JIS-K-7203. It was measured at a measuring temperature of 23°C at a loading speed of 2.0 mm/min or 2.5 mm/min using a specimen having a

thickness of 6.4 mm and a span length of 100 mm molded by injection molding.

(0136)

(13) Izod impact strength (Izod, unit: kg·cm/cm<sup>2</sup>)

It was measured according to a method defined in JIS-K-7110.

It was measured at a measuring temperature of 23°C or -30°C using a notched specimen subjected to a notch processing after molding, having a thickness of 6.4 mm molded by injection molding.

(0137)

(14) Heat deformation temperature (HDT, unit: °C)

It was measured according to a method defined in JIS-K-7207.

The fiber stress was measured at 18.6 kg/cm<sup>2</sup> or 4.6 kg/cm<sup>2</sup>.

(0138)

(15) Rockwell hardness (HR)

It was measured according to a method defined in JIS-K-7202.

It was measured using a specimen having a thickness of 3.0 mm molded by injection molding. The measured value was represented in R scale.

(0139)

(16) Flow mark appearance

A specimen of 100 mm×400 mm×3.0 mm (thickness) molded by injection molding was used, and the appearance thereof was observed visually, and judging between excellent and poor was conducted.

(0140)

## (17) Molded article granular structure appearance

A specimen of 100 mm×400 mm×3.0 mm (thickness) molded by injection molding was used, and the appearance thereof was observed visually.

(0141)

(Production of injection molded body)

(Production-1 of injection molded body)

The specimens, injection molded body for evaluation of physical properties in the above-mentioned items (11) to (15) were manufactured according to the following methods.

(1a) Specimens used in Examples 1 to 16 and Comparative Examples 1 to 13

A specimen, injection molded body, was obtained by effecting injection molding at a molding temperature of 220°C, a mold cooling temperature of 50°C, an injection time of 15 seconds, and a cooling time of 30 seconds, using an injection molding machine NEOMAT350/120 type manufactured by Sumitomo Heavy Industries, Ltd.

(1b) Specimens used in Examples 17 and 18 and Comparative Examples 14 and 15

A specimen, injection molded body, was obtained by effecting injection molding at a molding temperature of 220°C, a mold cooling temperature of 50°C, an injection time of 15 seconds, and a cooling time of 30 seconds, using an injection molding machine IS150E-V type manufactured by Toshiba Machine

Co., Ltd.

(0142)

(Production-2 of injection molded body)

The specimens, injection molded body for evaluation of appearance in the above-mentioned items (16) and (17) were manufactured according to the following method.

A specimen, injection molded body, was obtained by effecting injection molding at a molding temperature of 220°C, a mold cooling temperature of 50°C, an injection time of 15 seconds, and a cooling time of 30 seconds, using an injection molding machine NEOMAT515/150 type manufactured by Sumitomo Heavy Industries, Ltd.

(0143)

Methods of synthesizing three kinds of catalysts (solid catalyst components (I), (II) and (III)) used for polymerizing polymers used in examples and comparative examples are shown below.

(1) Solid catalyst component (I)

A 200 liter SUS reaction vessel equipped with a stirrer was purged with nitrogen, then, 80 liter of hexane, 6.55 mol of tetrabutoxytitanium, 2.8 mol of diisobutyl phthalate and 98.9 mol of tetraethoxysilane were placed in this to form a uniform solution. Then, 51 liter of a 2.1 mol/L solution of butylmagnesium chloride in diisobutyl ether was dropped gradually over 5 hours while keeping the temperature in the

reaction vessel at 5°C. After completion of dropping, the solution was stirred at 5°C for 1 hour and at room temperature for 1 hour, then, the solution was separated into solid and liquid at room temperature, and washed with 70 L of toluene three times. Subsequently, the amount of toluene was controlled so as to obtain a slurry concentration of 0.2 kg/L, then, the slurry was stirred at 105°C for 1 hour. Then, the slurry was cooled to 95°C, and to this was added 47.6 mol of diisobutyl phthalate, and they were reacted at 95°C for 30 minutes. After the reaction, the solution was separated into solid and liquid, and washed with toluene twice. Subsequently, the amount of toluene was controlled so as to obtain a slurry concentration of 0.4 kg/L, then, to this was added 3.1 mol of diisobutylphthalate, 8.9 mol of n-dibutyl ether and 274 mol of titanium tetrachloride, and they were reacted at 105°C for 3 hours. After completion of the reaction, the solution was separated into solid and liquid at the same temperature, then, washed with 90 L of toluene twice at the same temperature. The amount of toluene was controlled so as to obtain a slurry concentration of 0.4 kg/L, then, to this was added 8.9 mol of n-dibutyl ether and 137 mol of titanium tetrachloride, and they were reacted at 105°C for 1 hour. After completion of the reaction, the solution was separated into solid and liquid at the same temperature, then, washed with 90 L of toluene three times at the same temperature, then, further washed with 70 L hexane three times, then, dried under reduced pressure.

pressure, to obtain 11.4 kg of a solid catalyst component. The solid catalyst component contained 1.83% by weight of a titanium atom, 8.4% by weight of a phthalate, 0.30% by weight of an ethoxy group, and 0.20% by weight of a butoxy group. This solid catalyst component is hereinafter called solid catalyst component (I).

(0144)

#### (2) Solid catalyst component (II)

A 200 liter SUS reaction vessel equipped with a stirrer was purged with nitrogen, then, 80 liter of hexane, 6.55 mol of tetrabutoxytitanium, 2.8 mol of diisobutyl phthalate and 98.9 mol of tetraethoxysilane were placed in this to form a uniform solution. Then, 51 liter of a 2.1 mol/L solution of butylmagnesium chloride in diisobutyl ether was dropped gradually over 5 hours while keeping the temperature in the reaction vessel at 5°C. After completion of dropping, the solution was stirred for 1 hour at room temperature, then, the solution was separated into solid and liquid at room temperature, and washed with 70 L of toluene three times. Subsequently, the amount of toluene was controlled so as to obtain a slurry concentration of 0.6 kg/L, then, a mixture of 8.9 mol of n-dibutyl ether and 274 mol of titanium tetrachloride was added, then, to this was further added 20.8 mol of phthalic chloride, and they were reacted at 110°C for 3 hours. After completion of the reaction, the solution was washed with toluene twice at 95°C. Then, the slurry concentration was controlled to 0.6 kg/L,

then, to this was added 3.13 mol of diisobutyl phthalate, 8.9 mol of n-dibutyl ether and 137 mol of titanium tetrachloride, and they were reacted at 105°C for 3 hours. After completion of the reaction, the solution was separated into solid and liquid at the same temperature, then, washed with 90 L of toluene twice at 95°C. Subsequently, the slurry concentration was controlled to 0.6 kg/L, then, to this was added 8.9 mol of n-dibutyl ether and 137 mol of titanium tetrachloride, and they were reacted at 95°C for 1 hour. After completion of the reaction, the solution was separated into solid and liquid at the same temperature, then, washed with 90 L of toluene three times at the same temperature. Subsequently, the slurry concentration was controlled to 0.6 kg/L, then, to this was added 8.9 mol of n-dibutyl ether and 137 mol of titanium tetrachloride, and they were reacted at 95°C for 1 hour. After completion of the reaction, the solution was separated into solid and liquid at the same temperature, then, washed with 90 L of toluene three times at the same temperature, further, the solution was washed with 90 L of toluene three times, then, dried under reduced pressure, to obtain 11.0 kg of a solid catalyst component. The solid catalyst component contained 1.89% by weight of a titanium atom, 20% by weight of a magnesium atom, 8.6% by weight of a phthalate, 0.05% by weight of an ethoxy group, and 0.21% by weight of a butoxy group, and showed excellent granulated condition containing no fine powder. This solid catalyst

component is hereinafter called solid catalyst component (II).

(0145)

(3) Solid catalyst component (III)

A 200 liter SUS reaction vessel equipped with a stirrer was purged with nitrogen, then, 80 liter of hexane, 6.55 mol of tetrabutoxytitanium, and 98.9 mol of tetraethoxysilane were placed in this to form a uniform solution. Then, 50 liter of a 2.1 mol/L solution of butylmagnesium chloride in diisobutyl ether was dropped gradually over 4 hours while keeping the temperature in the reaction vessel at 20°C. After completion of dropping, the solution was stirred further for 1 hour at 20°C, then, the solution was separated into solid and liquid at room temperature, and washed with 70 L of toluene three times. Subsequently, the amount of toluene was controlled so as to obtain a slurry concentration of 0.4 kg/L, then, a mixture of 8.9 mol of n-dibutyl ether and 274 mol of titanium tetrachloride was added, then, to this was further added 20.8 mol of phthalic chloride, and they were reacted at 110°C for 3 hours. After completion of the reaction, the solution was washed with toluene three times at 95°C. Then, the slurry concentration was controlled to 0.4 kg/L, then, to this was added 3.13 mol of diisobutyl phthalate, 8.9 mol of n-dibutyl ether and 109 mol of titanium tetrachloride, and they were reacted at 105°C for 1 hour. After completion of the reaction, the solution was separated into solid and liquid at the same temperature, then,

washed with 90 L of toluene twice at 95°C. Subsequently, the slurry concentration was controlled to 0.4 kg/L, then, to this was added 8.9 mol of n-dibutyl ether and 109 mol of titanium tetrachloride, and they were reacted at 95°C for 1 hour. After completion of the reaction, the solution was separated into solid and liquid at the same temperature, then, washed with 90 L of toluene twice at the same temperature. Subsequently, the slurry concentration was controlled to 0.4 kg/L, then, to this was added 8.9 mol of n-dibutyl ether and 109 mol of titanium tetrachloride, and they were reacted at 95°C for 1 hour. After completion of the reaction, the solution was separated into solid and liquid at the same temperature, then, washed with 90 L of toluene three times at the same temperature, further, the solution was washed with 90 L of toluene three times, then, dried under reduced pressure, to obtain 12.8 kg of a solid catalyst component. The solid catalyst component contained 2.1% by weight of a titanium atom, 18% by weight of a magnesium atom, 60% by weight of a chlorine atom, 7.15% by weight of a phthalate, 0.05% by weight of an ethoxy group, and 0.26% by weight of a butoxy group, and showed excellent granulated condition containing no fine powder. This solid catalyst component is hereinafter called solid catalyst component (III).

(0146)

(Polymerization of polymer)

(1) Polymerization of propylene homopolymer (HPP)

## (1-1) Polymerization of HPP-1

## (1-1a) Preliminary polymerization

In a 3 liter SUS autoclave equipped with a stirrer, to sufficiently dehydrated and deaerated hexane was added 25 mmol/L of triethylammonium (hereinafter, abbreviated as TEA), cyclohexylethyldimethoxysilane (hereinafter, abbreviated as CHEDMS) as an electron donor at a ratio CHEDMS/TEA of 0.1 (mol/mol), and 15 g/L of the solid catalyst component (I), and preliminary polymerization was effected while feeding propylene continuously until the concentration thereof reached 2.5 g/g solid catalyst while keeping the temperature at 15°C or lower. The resulted previous polymer slurry was transferred to a 120 L SUS diluting chamber equipped with a stirrer and liquid butane sufficiently purified was added to this for dilution, and the solution was stored at temperatures of 10°C or lower.

(0147)

## (1-1b) Main polymerization

In a fluidized bed reaction vessel having a content volume of 1 m<sup>3</sup> equipped with a stirrer, propylene and water were so fed as to keep a polymerization temperature of 80°C, a polymerization pressure of 1.8 MPa and a hydrogen concentration in a gas phase portion of 7 vol%, and continuous gas phase polymerization was conducted while continuously feeding 62 mmol/h of TEA, 6.2 mmol/h of CHEDMS and 1.2 g/h of the previous

polym r slurry prepared in (1) as a solid catalyst component, giving a polymer at 20 kg/h. The resulted polymer has a limiting viscosity [ $\eta$ ]<sub>p</sub> of 0.90 dl/g, and an isotactic pentad fraction of 0.97.

(0148)

#### (1-2) Polymerization of HPP-2 to 6

Polymerization was conducted in the same manner as for HPP-1 except that the hydrogen concentration in a gas phase portion and the feeding amount of a solid catalyst component in the main polymerization were controlled so as to obtain polymers shown in Table 1. The analysis results of the resulted polymers are shown in Table 1.

(0149)

### (2) Polymerization of propylene-ethylene block copolymer (BCPP)

#### (2-1) Polymerization of BCPP-1

##### (2-1a) Preliminary polymerization

Preliminary polymerization was conducted in the same manner as for HPP-1.

##### (2-1b) Main polymerization

Two fluidized bed reaction vessels having a content volume of 1 m<sup>3</sup> equipped with a stirrer were placed in series, a propylene polymer portion was polymerization in the first vessel, then, transferred to the second vessel without deactivating the produced polymer, and a propylene-ethylene copolymer portion

was continuously polymerized in gas phase in the second vessel. In the first vessel in the former step, propylene and water were so fed as to keep a polymerization temperature of 80°C, a polymerization pressure of 1.8 MPa and a hydrogen concentration in a gas phase portion of 7.4 vol%, and under this condition, continuous gas phase polymerization was conducted while feeding 33 mmol/h of TEA, 3.3 mmol/h of CHEDMS and 0.8 g/h of the previous polymer slurry prepared in (1) as a solid catalyst component, giving 18.7 kg/h of a polymer. The polymer has a limiting viscosity  $[\eta]_p$  of 0.90 dl/g. The discharged produced polymer was fed continuously to the second vessel in the latter step. In the second vessel in the latter step, propylene, ethylene and hydrogen were continuously so fed as to keep a polymerization temperature of 65°C, a polymerization pressure of 1.4 MPa, a hydrogen concentration in a gas phase portion of 4.1 vol% and an ethylene concentration of 17.2 vol%, and under this condition, continuous polymerization was continued while feeding n-propymethyldimethoxysilane at 22 mmol/h, giving a polymer at 22.5 dl/g. The resulted polymer has a limiting viscosity  $[\eta]_T$  of 1.07 dl/g, and the polymer content (EP content) in the latter step portion was 17% by weight, therefore, the polymer produced in the latter step portion (EP portion) has a limiting viscosity  $[\eta]_{EP}$  of 1.9 dl/g. As a result of analysis, the ethylene content in the EP portion was 40% by weight.

(0150)

## (2-2) Polymerization of BCPP-2 and BCPP-3

Polymerization was conducted in the same manner as for BCPP-1 except that the hydrogen concentration in a gas phase portion, the ethylene content and the feeding amount of a solid catalyst component in the main polymerization were controlled so as to obtain polymers shown in Table 2. The analysis results of the resulted polymers are shown in Table 2.

(0151)

$[\eta]$ , shown in Table 1,  $[\eta]_P$ ,  $[\eta]_{EP}$ , ethylene content in EP and EP content shown in Table 2 are obtained by analyzing powders of propylene homopolymers (HPP-1 to HPP-6) and propylene-ethylene block copolymer (BCPP-1 to BCPP-3) obtained by the above-mentioned polymerization, respectively, and MFR is a MFR of a pellet prepared by adding 0.05 parts by weight of calcium stearate (manufactured by NOF Corp.) as a stabilizer, 0.05 parts by weight of

3,9-bis[2-{3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionyl oxy}-1,1-dimethylethyl]-2,4,8,10-tetraoxaspiro[5.5]undecane (Sumilizer GA80, manufactured by Sumitomo Chemical Co., Ltd.) and 0.05 parts by weight of

bis(2,4-di-t-butylphenyl)pentaerythritol diphosphite (Ultranox U626, manufactured by GE Speciality Chemicals) to 100 parts by weight of a powder and granulating the mixture, using a  $\phi$  40 mm single-screw extruder ( $220^{\circ}\text{C}$ , screen pack: 100 mesh).

(0152)

(3) Polymerization of propylene-based polymer component

(A1)(HMS)

(3-1) Polymerization of HMS-1

After drying under reduced pressure, into a nitrogen-purged stainless autoclave having a content volume of 3 liter equipped with a stirrer was charged 5.1 mg of the above-mentioned solid catalyst component (II), 8.8 mmol of TEA and 88.1  $\mu$ mol of ditertiarybutyl dimethoxysilane as an electron donor component after they were allowed to contact in a heptane solution in a glass charger previously. Further, 50 mmHg of hydrogen and 780 g of propylene were charged into the above-mentioned autoclave and the mixture was heated up to 80°C to initiate polymerization. Directly after temperature rising to 80°C, an ethylene gas was continuously fed so as to give an ethylene partial pressure of 0.1 kg/m<sup>2</sup>G and polymerization was conducted for 60 minutes. 60 minutes after, the gas in the autoclave was purged, and the produced polymer was dried at 60°C for 5 hours under reduce pressure, to obtain 198.3 g of a polymer powder. The resulted powder had a limiting viscosity of 7.6 (dl/g) and an ethylene content of 2.7% by weight. The melting temperature peak T<sub>m</sub> was 148.1°C. The analysis results of the resulted HMS-1 are shown in Table 3.

(0153)

(3-2) Polymerization of HMS-2

Polymerization was conducted in the same manner as for HMS-1 except that the amount of the solid catalyst component (II) was changed to 5.0 mg, the hydrogen addition amount was changed to 110 mmHg and the ethylene partial pressure during polymerization was changed to 0.2 kg/m<sup>2</sup>G. The amount of the resulted polymer was 410.5 g, the limiting viscosity was 5.8 (dl/g) and the ethylene content was 4.5% by weight. The melting temperature peak T<sub>m</sub> was 137.5°C. The analysis results of the resulted HMS-2 are shown in Table 3.

(0154)

### (3-3) Polymerization of HMS-3

#### (3-3a) Preliminary polymerization

In a 3 liter SUS autoclave equipped with a stirrer, to sufficiently dehydrated and deaerated hexane was added triethylammonium (hereinafter, abbreviated as TEA) at 25 mmol/L, t-butyl-n-propyldimethoxysilane (hereinafter, abbreviated as tBunPrDMS) as an electron donor component at a ratio tBunPrDMS/TEA of 0.1 (mol/mol), and the solid catalyst component (III) at 15 g/L, and preliminary polymerization was effected while feeding propylene continuously until the concentration thereof reached 1 g/g solid catalyst while keeping the temperature at 15°C or lower. The resulted previous polymer slurry was transferred to a 120 L SUS diluting chamber equipped with a stirrer and liquid butane sufficiently purified was added to this for dilution, and the solution was stored at temperatures

of 10°C or lower.

#### (3-3b) Main polymerization

In a 300 liter SUS autoclave equipped with a stirrer, liquefied propylene was so fed at a rate of 35 kg/h as to keep a polymerization temperature of 60°C and a slurry amount of 95 L, further, liquid 1-butene was fed so as to keep a 1-butene concentration in a gas phase portion of 15.6 vol%, and continuous copolymerization of propylene-1-butene was conducted while feeding TEA at 31 mmol/h, tBunPrDMS at 4.7 mmol/h and the previous polymer slurry prepared in (3-a) as a solid catalyst component at 1.3 g/h, giving a polymer at 4.6 kg/h. The resulted polymer has a limiting viscosity [ $\eta$ ] of 7.0 dl/g, a 1-butene content of 13.6% by weight, and a melting peak temperature of 152.5°C. The analysis results of the resulted HMS-3 are shown in Table 3.

(0155)

#### (3-4) Polymerization of HMS-4

##### (3-4a) Preliminary polymerization

Preliminary polymerization was conducted in the same manner as for HMS-3.

##### (3-4b) Main polymerization

In a 300 liter SUS autoclave equipped with a stirrer, liquefied propylene was so fed at a rate of 45 kg/h as to keep a polymerization temperature of 60°C and a slurry amount of 95 L, further, liquid 1-butene was fed so as to keep a 1-butene

concentration in a gas phase portion of 5.5 vol%, and continuous copolymerization of propylene-1-butene was conducted while feeding TEA at 31 mmol/h, tBunPrDMS at 4.7 mmol/h and the previous polymer slurry prepared in (3-4a) as a solid catalyst component at 1.5 g/h, giving a polymer at 4.0 kg/h. The resulted polymer has a limiting viscosity [ $\eta$ ] of 5.1 dl/g, a 1-butene content of 5.1% by weight, and a melting peak temperature of 154.0°C. The analysis results of the resulted HMS-3 are shown in Table 3.

(0156)

#### (3-5) Polymerization of HMS-5

##### (3-5a) Preliminary polymerization

Preliminary polymerization was conducted in the same manner as for HMS-3.

##### (3-5b) Main polymerization

In a 300 liter SUS autoclave equipped with a stirrer, liquefied propylene was fed at a rate of 50 kg/h as to keep a polymerization temperature of 60°C and a slurry amount of 95 L, and continuous polymerization of propylene was conducted while feeding TEA at 31 mmol/h, tBunPrDMS at 4.5 mmol/h and the previous polymer slurry prepared in (3-5a) as a solid catalyst component at 1.3 g/h, giving a polymer at 2.6 kg/h. The resulted polymer has a limiting viscosity [ $\eta$ ] of 7.9 dl/g and a melting peak temperature of 164.8°C. The analysis results of the resulted HMS-5 are shown in Table 3.

(0157)

(3-6) Polymerization of HMS-6

(3-6a) Preliminary polymerization

Preliminary polymerization was conducted in the same manner as for HPP-1 except that the solid catalyst component (II) was used and tBunPrDMS was used as the electron donor compound.

(3-6b) Main polymerization

In an SUS gas phase fluidized bed reaction vessel having a content volume of 1 m<sup>3</sup> equipped with a stirrer, propylene, hydrogen and ethylene were so fed as to keep a polymerization temperature of 60°C, a polymerization pressure of 1.8 MPa, a hydrogen concentration in a gas phase portion of 0.1 vol% and an ethylene concentration in a gas phase portion of 7.3 vol%, and continuous gas phase polymerization of propylene-ethylene was conducted while feeding TEA at 60 mmol/h, tBunPrDMS at 6 mmol/h and the previous polymer slurry prepared in (3-6a) as a solid catalyst component at 0.9 g/h, giving a polymer at 22.5 kg/h. The resulted polymer has a limiting viscosity [ $\eta$ ] of 5.3 dl/g, an ethylene content of 9.6% by weight and a melting temperature peak of 115.6°C. The analysis results of the resulted HMS-6 are shown in Table 3.

(0158)

(3-7) Polymerization of HMS-7

(3-7a) Preliminary polymerization

Preliminary polymerization was conducted in the same manner as for HMS-3 except that the solid catalyst component (I) was used.

### (3-7b) Main polymerization

In a 300 liter SUS autoclave equipped with a stirrer, liquefied propylene was so fed at a rate of 35 kg/h as to keep a polymerization temperature of 60°C and a slurry amount of 95 L. further, ethylene was fed so as to keep an ethylene concentration in a gas phase portion of 2.9 vol%, and continuous copolymerization of propylene-ethylene was conducted in the substantial absence of hydrogen while feeding TEA at 51 mmol/h, tBunPrDMS at 5 mmol/h and the previous polymer slurry prepared in (3-7a) as a solid catalyst component at 1.0 g/h, giving a polymer at 6.5 kg/h. The resulted polymer was transferred continuously to the second vessel without deactivation. In the second vessel, SUS fluidized bed gas phase reaction vessel having a content volume of 1 m<sup>3</sup> equipped with a stirrer, propylene and water were so fed as to keep a polymerization temperature of 70°C, a polymerization pressure of 0.8 MPa and an ethylene concentration in a gas phase portion of 1.8 vol%, and continuous gas phase polymerization was continued using the solid catalyst component-containing polymer transferred from the first vessel in the substantial absence of hydrogen, giving a polymer at 16.3 kg/h. The polymer had a limiting viscosity [ $\eta$ ] of 8.4 dl/g, an ethylene content of 3.4% by weight and a melting

temperature peak of 144.8°C. The analysis results of the resulted HMS-7 are shown in Table 3.

(0159)

(3-8) Polymerization of HMS-8

(3-8a) Preliminary polymerization

Preliminary polymerization was conducted in the same manner as for HMS-3 except that the solid catalyst component (I) was used.

(3-8b) Main polymerization

In a 300 liter SUS polymerization vessel equipped with a stirrer, liquefied propylene was so fed at a rate of 35 kg/h as to keep a polymerization temperature of 60°C and a slurry amount of 95 L, further, liquid 1-butene was fed so as to keep a 1-butene concentration in a gas phase portion of 10.1 vol%, and continuous copolymerization of propylene-1-butene was conducted in the substantial absence of hydrogen while feeding TEA at 53 mmol/h, tBunPrDMS at 4.7 mmol/h and the previous polymer slurry prepared in (3-8a) as a solid catalyst component at 1.7 g/h, giving a polymer at 4.4 kg/h. The resulted polymer has a limiting viscosity [ $\eta$ ] of 8.4 dl/g, a 1-butene content of 7.4% by weight, and a melting peak temperature of 149.8°C. The analysis results of the resulted HMS-8 are shown in Table 3.

(0160)

(3-9) Polymerization of HMS-9

(3-9a) Preliminary polymerization

Preliminary polymerization was conducted in the same manner as for HMS-3 except that the solid catalyst component (I) was used.

(3-9b) Main polymerization

In a 300 liter SUS polymerization vessel equipped with a stirrer, liquefied propylene was so fed at a rate of 35 kg/h as to keep a polymerization temperature of 60°C and a slurry amount of 95 L, further, ethylene was fed so as to keep an ethylene concentration in a gas phase portion of 2.8 vol%, and continuous copolymerization of propylene-ethylene was conducted in the substantial absence of hydrogen while feeding TEA at 51 mmol/h, tBunPrDMS at 5 mmol/h and the previous polymer slurry prepared in (3-9a) as a solid catalyst component at 1.0 g/h, giving a polymer at 6.1 kg/h. The resulted polymer was transferred continuously to the second vessel without deactivation. In the second vessel, SUS fluidized bed gas phase reaction vessel having a content volume of 1m<sup>3</sup> equipped with a stirrer, propylene and ethylene were so fed as to keep a polymerization temperature of 70°C, a polymerization pressure of 1.8 MPa and an ethylene concentration in a gas phase portion of 1.9 vol%, and continuous gas phase polymerization was continued using the solid catalyst component-containing polymer transferred from the first vessel in the substantial absence of hydrogen, giving a polymer at 15.7 kg/h. The resulted polymer corresponds to a propylene-based polymer component (A1), and has a limiting

viscosity [ $\eta$ ] of 8.7 dl/g, an ethylene content of 3.5% by weight, and a melting temperature peak of 144.8°C, and the analysis results are shown in Table 3. Subsequently, the resulted polymer was transferred continuously to the third vessel without deactivation. In the third vessel, SUS gas phase fluidized bed reaction vessel having a content volume of 1 m<sup>3</sup> equipped with a stirrer, propylene and hydrogen were so fed as to keep a polymerization temperature of 85°C, a polymerization pressure of 1.4 MPa and a hydrogen concentration in a gas phase portion of 11.7 vol%, and continuous gas phase polymerization was continued using the polymer containing a solid catalyst component fed from the second vessel, giving a polymer at 25.6 kg/h. The resulted polymer is HMS-9 and corresponds to a propylene-based polymer composition (E), and has a limiting viscosity [ $\eta$ ] of 5.7 dl/g. From the above-mentioned results, it was determined that the ratio of the total polymerization amount of the first vessel and the second vessel to the polymerization amount of the third vessel was 61:39, and the polymer produced in the third vessel had a limiting viscosity [ $\eta$ ] of 0.9 dl/g.

(0161)

#### (3-10) Polymerization of HMS-10

The polymerization was conducted in the same manner as for HMS-9 except that the ethylene concentration in a gas phase portion and the feeding amount of a solid catalyst component

in the first vessel and second vessel and the hydrogen concentration in a gas phase portion in the third vessel were changed, to obtain HMS-10 corresponding to a propylene-based polymer composition (E). The polymer produced up to the second vessel corresponds to a propylene-based polymer (A1), and has a limiting viscosity [ $\eta$ ] of 8.2 dl/g, an ethylene content of 2.0% by weight and a melting temperature peak of 150.8°C, and the analysis results are shown in Table 3. The ratio of the total polymerization amount of the first vessel and the second vessel to the polymerization amount of the third vessel was 60:40, and the polymer produced in the third vessel had a limiting viscosity [ $\eta$ ] of 1.1 dl/g.

(0162)

### (3-11) Polymerization of HMS-11

The polymerization was conducted in the same manner as for HMS-10 except that the comonomer fed to the first vessel and second vessel was changed to 1-butene and the 1-butene concentration in a gas phase portion and the feeding amount of a solid catalyst component were controlled, to obtain HMS-11 corresponding to a propylene-based polymer composition (E). The polymer produced up to the second vessel corresponds to a propylene-based polymer (A1), and has a limiting viscosity [ $\eta$ ] of 7.6 dl/g, a 1-butene content of 6.5% by weight and a melting temperature peak of 150.7°C, and the analysis results are shown in Table 3. The ratio of the total polymerization

amount of the first vessel and the second vessel to the polymerization amount of the third vessel was 47:53, and the polymer produced in the third vessel had a limiting viscosity [ $\eta$ ] of 1.1 dl/g.

(0163)

### (3-12) Polymerization of HMS-12

The polymerization was conducted in the same manner as for HMS-11 except that 1-butene concentration in a gas phase portion and the feeding amount of a solid catalyst component in the first vessel and second vessel were controlled, to obtain HMS-12 corresponding to a propylene-based polymer composition (E). The polymer produced up to the second vessel corresponds to a propylene-based polymer (A1), and has a limiting viscosity [ $\eta$ ] of 7.3 dl/g, a 1-butene content of 8.2% by weight and a melting temperature peak of 148.0°C, and the analysis results are shown in Table 3. The ratio of the total polymerization amount of the first vessel and the second vessel to the polymerization amount of the third vessel was 45:55, and the polymer produced in the third vessel had a limiting viscosity [ $\eta$ ] of 1.1 dl/g.

(0164)

#### Example-1

0.05 parts by weight of calcium stearate (manufactured by NOF Corp.) as a stabilizer, 0.05 parts by weight of 3,9-bis[2-{3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionyl

oxy)-1,1-dimethylethyl]-2,4,8,10-tetraoxaspiro[5.5]undecane (Sumilizer GA80, manufactured by Sumitomo Chemical Co., Ltd.) and 0.05 parts by weight of bis(2,4-di-t-butylphenyl)pentaerythritol diphosphite (Ultranox U626, manufactured by GE Speciality Chemicals) were added to 100 parts by weight of a resin composition composed of 20% by weight of a propylene homopolymer powder (HPP-5), 75% by weight of a propylene homopolymer powder (HPP-6) and 5% by weight of a propylene-based polymer powder (HMS-1), and they were dry-blended, then, granulated three times by a  $\phi$  40 mm single-screw extruder (220°C, screen pack: metal fiber-sintered filter NF13D manufactured by Nippon Seisen), to obtain a polypropylene-based resin composition. Table 4 shows compounding ratios of components, evaluation results of MFR, die swell of polypropylene-based resin compositions obtained by granulation, number-1 of granular structures (number of granular structures having a size of 200  $\mu\text{m}$  or more observed per 10  $\text{cm}^2$  of a film) and mechanical properties.

(0165)

#### Examples 2 to 4

Dry blend was effected in the same manner as in Example 1 using compounding ratios of components shown in Table 4, then, granulation was conducted to obtain polypropylene-based resin compositions. The evaluation results of MFR, die swell, number-1 of granular structures (number of granular structures

having a size of 200  $\mu\text{m}$  or more observed per 10  $\text{cm}^2$  of a film) and mechanical properties are shown in Table 4.

(0166)

#### Comparative Examples 1 to 4

Dry blend was effected in the same manner as in Example 1 using compounding ratios of components shown in Table 5, then, granulation was conducted to obtain polypropylene-based resin compositions. The evaluation results of MFR, die swell, number-1 of granular structures (number of granular structures having a size of 200  $\mu\text{m}$  or more observed per 10  $\text{cm}^2$  of a film) and mechanical properties are shown in Table 5.

(0167)

#### Example-5

0.05 parts by weight of calcium stearate (manufactured by NOF Corp.) as a stabilizer, 0.05 parts by weight of 3,9-bis[2-(3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionyl oxy)-1,1-dimethylethyl]-2,4,8,10-tetraoxaspiro[5.5]undecane (Sumilizer GA80, manufactured by Sumitomo Chemical Co., Ltd.) and 0.05 parts by weight of bis(2,4-di-t-butylphenyl)pentaerythritol diphosphite (Ultrinox U626, manufactured by GE Speciality Chemicals) were added to 100 parts by weight of a resin composition composed of a mixture (iii) of 65% by weight of a propylene-ethylene block copolymer (i) powder (BCPP-1) and 30% by weight of a propylene homopolymer powder (HPP-5), and 5% by weight of a

propylene-based polymer component (MB-1), and they were dry-blended, then, granulated by a  $\phi$  40 mm single-screw extruder (220°C, screen pack: metal fiber-sintered filter NF13D manufactured by Nippon Seisen), to obtain a polypropylene-based resin composition.

(0168)

The above-mentioned propylene-based polymer composition (MB-1) is a propylene-based polymer composition obtained by adding 0.05 parts by weight of calcium stearate (manufactured by NOF Corp.) as a stabilizer, 0.05 parts by weight of 3,9-bis[2-{3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionyl oxy}-1,1-dimethylethyl]-2,4,8,10-tetraoxaspiro[5.5]undecane (Sumilizer GA80, manufactured by Sumitomo Chemical Co., Ltd.) and 0.05 parts by weight of bis(2,4-di-t-butylphenyl)pentaerythritol diphosphite (Ultranox U626, manufactured by GE Speciality Chemicals) to 100 parts by weight of a resin composition composed of 50% by weight of a propylene homopolymer powder (HPP-5) and 50% by weight of a propylene-based polymer powder mainly composed of propylene (HMS-7), dry-blending them, then granulation the by a  $\phi$  40 mm single-screw extruder (220°C, screen pack: #100 wire mesh), and corresponds to a propylene-based polymer composition (E). Table 6 shows evaluation results of MFR, die swell and number-1 of granular structures (number of granular structures having a size of 200  $\mu\text{m}$  or more observed per 10  $\text{cm}^2$  of a film)

of polypropylene-based resin compositions obtained by granulation at compounding ratios of components shown in Table 6.

(0169)

Examples 6 to 14

The evaluation results of MFR, die swell and number-1 of granular structures (number of granular structures having a size of 100  $\mu\text{m}$  or more and 200  $\mu\text{m}$  or more observed per 10  $\text{cm}^2$  of a film) of polypropylene-based resin compositions obtained by dry-blending in the same manner as in Example-5 at compounding ratios of components shown in Table 6 (Examples 6 to 9) or Table 7 (Examples 10 to 14) and granulating them, are shown in Table 6 (Examples 6 to 9) or Table 7 (Examples 10 to 14), respectively.

(0170)

(MB-2) and (MB-3) used in Examples 6 to 9 are resin compositions shown below, and correspond to a propylene-based polymer composition (E).

(MB-2):

A resin composition composed of 50% by weight of a propylene homopolymer powder (HPP-5) and 50% by weight of a propylene-based polymer powder (HMS-8)

(MB-3):

A resin composition composed of 50% by weight of a propylene homopolymer powder (HPP-5) and 50% by weight of a propylene-based polymer powder (HMS-8)

polymer powder (HMS-3)

The above-mentioned (MB-2) and (MB-3) were obtained by pelletizing by the same granulation method using the same stabilizer as for (MB-1) in Example 5.

(0171)

Comparative Examples 5 to 12

The evaluation results of MFR, die swell and number-1 of granular structures (number of granular structures having a size of and 200  $\mu\text{m}$  or more observed per 10  $\text{cm}^2$  of a film) of polypropylene-based resin compositions obtained by dry-blending in the same manner as in Example-5 at compounding ratios of components shown in Table 8 (Comparative Examples 5 to 8) or Table 9 (Comparative Examples 9 to 12) and granulating them, are shown in Table 8 (Comparative Examples 5 to 8) or Table 9 (Comparative Examples 9 to 12), respectively.

(0172)

(MB-4) used in Comparative Examples 5 to 8 is resin composition shown below, and correspond to a propylene-based polymer composition (E).

(MB-4):

A resin composition composed of 50% by weight of a propylene homopolymer powder (HPP-5) and 50% by weight of a propylene-based polymer powder (HMS-5)

The above-mentioned (MB-4) was obtained by pelletizing by the same granulation method using the same stabilizer as

for (MB-1) in Example 5.

(0173)

Example 15

To 100 parts by weight of a resin composition composed of 60% by weight of the polypropylene-based resin composition described in Example 1, 6% by weight of a propylene homopolymer (F) powder (HPP-4), 14% by weight of an ethylene-octene-1 random copolymer (EOR) having an octene-1 content of 24% by weight and a melt flow rate (MFR, JIS-K-6758, 190°C) of 5 g/10 minutes as an elastomer (G) and 20% by weight of talc having an average particle size of 2.5 μm as an elastomer (G), was added the same stabilizer as used in Example 5, and the mixture was uniformly mixed previously in a tumbler, then, the mixture was kneaded and extruded under vent suction using a twin-screw extruder (TEX44SS 30BW-2V type, manufactured by The Japan Steel Works Ltd.) at an extrusion rate of 30 to 50 kg/hr and a screw revolution of 350 rpm, to produce a polypropylene-based resin composition. The screw was so constituted that a three blade type rotor and a kneading disk were placed at the first feeding port, and the next zone to the second feeding port, namely, two positions in the kneading zone.

(0174)

Compounding ratios of components, and the evaluation results of MFR, die swell, flow mark, granular structure appearance and mechanical properties of the resulted

polypropylene-based resin composition are shown in Table 10.

(0175)

**Example 16**

Polymerization was conducted in the same manner as in Example 15 except that the polypropylene-based resin composition used in Example 15 was changed to the polypropylene-based resin composition described in Example 10.

Compounding ratios of components, and the evaluation results of MFR, die swell, flow mark, granular structure appearance and mechanical properties of the resulted polypropylene-based resin composition are shown in Table 10.

(0176)

**Comparative Examples 13 and 14**

Polymerization was conducted in the same manner as in Example 15 except that the polypropylene-based resin composition used in Example 15 was changed to the polypropylene-based resin composition described in Comparative Example 5 or Comparative Example 9.

Compounding ratios of components, and the evaluation results of MFR, die swell, flow mark, granular structure appearance and mechanical properties of the resulted polypropylene-based resin composition are shown in Table 10.

(0177)

(Table 1)

		$[\eta]_P$	MFR
		dl/g	g/10 minutes
Propylene homopolymer	HPP-1	0.90	140
	HPP-2	0.84	195
	HPP-3	1.48	11
	HPP-4	1.21	29
	HPP-5	0.92	120
	HPP-6	1.34	17

(0178)

(Table 2)

		$[\eta]_P$	$[\eta]_{EP}$	Ethylene content in EP	EP content	MFR
		dl/g	dl/g	wt%	wt%	g/10 minutes
Ethylene-p ropylene block copolymer	BCPP-1	0.90	1.9	40	17	68
	BCPP-2	0.92	2.5	55	13	64
	BCPP-3	0.81	2.1	57	12	128

(0179)

(Table 3)

	[η] <sup>A1</sup>	Tm <sup>A1</sup>
	dl/g	°C
Propylene-based polymer component (A1)	HMS-1	7.6
	HMS-2	5.8
	HMS-3	7.0
	HMS-4	5.1
	HMS-5	7.9
	HMS-6	5.3
	HMS-7	8.4
	HMS-8	8.4
	HMS-9	8.7
	HMS-10	8.2
	HMS-11	7.6
	HMS-12	7.3

(0180)

(Table 4)

		Example			
		1	2	3	4
Composition (wt%)	HPP-5	20	20		
	HPP-6	75	75	95	95
	HMS-1	5			
	HMS-2		5		
	HMS-3			5	
	HMS-4				5
Mw/Mn				4.0	3.7
MFR g/10 minutes		15	16	11	12
Die swell		2.14	1.92	2.04	1.79
UE(50mm/minutes) %		739	637	725	733
UE(70mm/minutes) %		108	572	769	751
FM(2.5mm/minutes) kg/cm <sup>2</sup>		15200	14600	14700	14500
HDT(4.6kg/cm <sup>2</sup> ) °C		118	111	117	120
IZOD23°C kg·cm/cm		2.1	2.0	2.2	2.0
Number-1 of granular structure		3	4	0	0
structures/10 cm <sup>2</sup>					

(0181)

(Table 5)

		Comparative example			
		1	2	3	4
Composition (wt%)	HPP-6	95	95	100	
	HPP-7				100
	HMS-5	5			
	HMS-6		5		
Mw/Mn		3.9	3.8	3.3	
MFR	g/10 minutes	10	12	17	11
Die swell		2.12	1.76	1.63	1.57
UE(50mm/minutes)	%	730	631	322	766
UE(70mm/minutes)	%	21	709	38	744
FM(2.5mm/minutes)	kg/cm <sup>2</sup>	15000	13700	14800	14500
HDT(4.6kg/cm <sup>2</sup> )	℃	116	117	110	114
IZOD23℃	kg·cm/cm	2.7	2.7	2.1	2.1
Number-1 of granular structure	structures/10 cm <sup>2</sup>	0	0	-	-

(0182)

(Table 6)

		Example				
		5	6	7	8	9
Composition (wt%)	(D)	BCPP-1	65	65		
		BCPP-2			55	55
		BCPP-3			10	10
		HPP-5	30	30	30	27
		HPP-2				27
	(E)	MB-1	5			
		MB-2		5		
		MB-3			5	8
	MFR	g/10 minutes	56	53	55	45
	Die swell		2.13	2.09	2.05	2.22
Number-1 of granular structure	structures/10 cm <sup>2</sup>	3	1	2	3	4

(0183)

(Table 7)

			Example				
			10	11	12	13	14
Composition  (D) wt%	BCPP-1	65	65	65	65		
							55
							15
		HPP-5	30	30	30	30	25
		HPP-2					
	HMS-9  (E) wt%	5					5
			5				
				5			
		HMS-12				5	
MFR	g/10 minutes	50	60	68	58	53	
Die swell		2.15	2.17	2.13	2.11	2.21	
Number-1 of granular structure	number/10 cm <sup>2</sup>	5	3	1	1	2	

(0184)

(Table 8)

			Comparative example			
			5	6	7	8
Composition  (D) wt%	BCPP-1	65				
			55	55		
			10	10	65	
		30	30	27		
					27	
	MB-4  (E)	5	5	8	8	
		63	57	47	77	
		2.08	206	2.32	2.34	
Number-1 of granular structure	structures/10 cm <sup>2</sup>	8	26	15	8	

(0185)

(Table 9)

		Comparative example				
		9	10	11	12	
Composition (wt%)	(D)	BCPP-1	65	65		
		BCPP-2			65	
		BCPP-3			65	
		HPP-5	7			
		HPP-2	28		35	
		HPP-1		35	35	
MFR g/10 minutes		67	85	84	148	
Die swell		1.39	1.40	1.37	1.36	
Number-1 of granular structure structures/10 cm <sup>2</sup>		0	1	1	0	

(0186)

(Table 10)

		Example		Comparative example		
		15	16	13	14	
Compo- sition (wt%)	Resin compo- sition	Example 5	60			
		Example 10		60		
		Comparative example 5			60	
		Comparative example 9			60	
		(F) HPP-4	6	6	6	
		(G) EOR	14	14	14	
(H) talc		20	20	20	20	
MFR g/10 minutes		28.4	28.2	29.8	29.3	
Die swell		1.51	1.51	1.50	1.25	
Flow mark appearance visual observation		good	good	good	poor	
Molded article granular structure appearance visual observation		○	○	△	○	
Number-2(>200) of granular structure structures/43cm <sup>2</sup>		0	0	4	0	
YS kg/cm <sup>2</sup>		241	244	245	238	
UE(10mm/minutes) %		375	457	96	498	
FM(2.0mm/minutes) kg/cm <sup>2</sup>		22300	22700	22700	22200	
IZOD 23°C kg·cm/cm		20	19.9	17.3	19.9	
IZOD -30°C kg·cm/cm		2.5	2.4	2.4	2.5	
HDT(18.6kg/cm <sup>2</sup> ) °C		75	76	76	76	
HR R scale		72	72	73	74	

Molded article granular structure appearance visual  
observation

○: Existence of granular structure was not recognized

△: Existence of granular structure was slightly  
recognized

(0187)

It is understood that the compositions of Examples 1 to 16 satisfying the conditions of the present invention, when processed into a molded article, show a low tendency of generation of flow mark, namely, have excellent appearance such as high die swell, generation of little granular structure and the like, and are excellent in balance between rigidity and toughness.

(0188)

On the other hand, it is understood that the composition of Comparative Example 1 shows low tensile elongation (UE) since the melting temperature peak  $T_m^{A1}$  of a propylene-based polymer component (A1) does not satisfy the requirement of the invention, the composition of Comparative Example 2 shows low flexural modulus (FM) since the melting temperature peak  $T_m^{A1}$  of a propylene-based polymer component (A1) does not satisfy the requirement of the invention, and the compositions of Comparative Examples 3 and 4 show low die swell and have insufficient balance between flowability (MFR) and tensile elongation (UE) since a propylene-based polymer component (A1) is not contained in the compositions.

(0189)

Further, it is understood that the compositions of Comparative Examples 5 to 8 give a lot of granular structure since they do not satisfy the requirement of the invention,

and the compositions of Comparative Examples 9 to 12 manifest low die swell since a propylene-based polymer component (A1) is not contained in the compositions.

(0190)

It is understood that the composition of Comparative Example 13 shows low tensile elongation (UE) since the melting temperature peak  $T_m^{A1}$  of a propylene-based polymer component (A1) does not satisfy the requirement of the invention, and the composition of Comparative Example 14 shows low die swell and manifests poor flow mark appearance since a propylene-based polymer component (A1) is not contained in the composition.

(0191)

(Effect of the Invention)

As described in detail above, a polypropylene-based resin composition which, when made into a molded body, has a low tendency of generation of flow marks, namely, has excellent appearance such as low die swell, little generation of granular structures and the like, and is excellent in balance of rigidity and toughness, a method of producing the same and an injection molded body made of the same can be obtained according to the present invention.

[Document name] Abstract

[Abstract]

[Problem]

To provide a polypropylene-based resin composition which, when made into a molded body, has a low tendency of generation of flow marks, namely, has excellent appearance such as low die swell, little generation of granular structures and the like, and is excellent in balance of rigidity and toughness, a method of producing the same and an injection molded body made of the same.

[Solution]

A polypropylene-based resin composition comprising a propylene-based polymer component obtained by polymerizing a monomer mainly composed of propylene, having limiting viscosity in a specific range and a melting temperature peak in a temperature rising thermogram by a differential scanning calorimeter (DSC) in a specific range and of which content is in a certain range and a propylene-based polymer component obtained by polymerizing a monomer mainly composed of propylene, having limiting viscosity in a specific range and of which content is in a certain range, a method of producing the same, and an injection molded body made of the same.

[Drawing Selected] None

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